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CXIX. *Fluorescent Secondary X-Radiation and the J-Phenomenon.*

By W. H. WATSON, *M.A., Ph.D., Lecturer in Natural Philosophy, University of Edinburgh* *.

Introduction.

THE study of the absorption of the secondary X-radiation from light substances has hitherto been the most successful means of investigating the J-phenomenon. It is obviously desirable that this study should be extended to the secondary radiation from substances whose characteristic radiation of K-series is excited by the primary beam. Some years ago † measurements were, in fact, made to determine the absorption coefficients in copper and aluminium of the whole characteristic radiation from a series of elements, the exciting primary beam being adjusted in hardness so as to produce the optimum emission of characteristic radiation (K-series) from the radiator. The results of the experiments were inconclusive, and actually it appears from recent work that the method of experiment adopted then is not the most suitable to exhibit "J" absorption effects.

In a recent paper on the J-phenomenon ‡, experiments were described in which the difficulties of control were surmounted sufficiently well to allow of consistent measurements which exhibited the "J" absorption effect in the transmission of the secondary radiation from paraffin-wax

* Communicated by Prof. C. G. Barkla, F.R.S.
† W. H. Watson, Ph.D. Thesis, 1925.
‡ C. G. Barkla and W. H. Watson, Phil. Mag., Nov. 1926.

through aluminium. Some further experiments of the same nature have since been made, and the results are put on record here, although the main investigation to be reported is concerned with the use of radiators of higher atomic number.

1. *Experimental Control.*

The main requirements for adequate control of the X-ray tube were stated in the paper referred to * :

(1) The peak voltage applied to the Coolidge tube should be maintained constant ; and
(2) The current through the X-ray tube should be kept steady.

When radiators of silver and tin were first employed about a year ago, it became clear that, even if the above conditions were carefully maintained, consistent results were obtained only when the X-ray tube was run into a steady state before measurements were made, and throughout the experiment was allowed to function continuously, the X-rays being shut off when desired by means of a shutter in the primary beam.

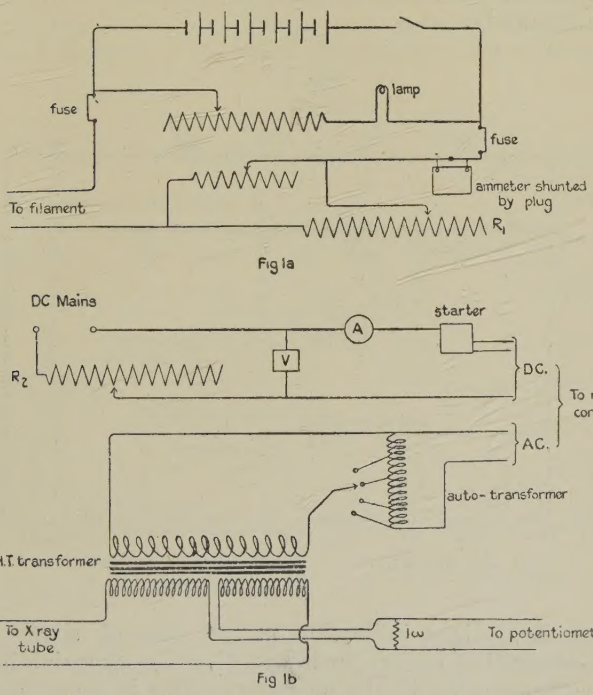
It should be clearly understood, therefore, that in the experiments to be described the results recorded here were obtained consistently, only when the X-ray tube was employed as a constant source of radiation, and that when this method of procedure was departed from, the only type of consistent result obtained was that got by making readings in a definite time order.

The arrangements for the control of the Coolidge X-ray tube are made clear in the diagrams. In fig. 1 *a* the rheostat R_1, operated by means of an insulating handle, is used to adjust the filament current when the tube is working. The power for high tension is supplied from the direct current mains (230 volts) through a rheostat R_2 (fig. 1 *b*) to a rotary converter (2 kw., 50 cycles), from which the alternating current is passed through an auto-transformer tapped suitably to operate the high-tension transformer (Watson & Sons, Ltd. ; 2 kw. 60 kv.). The secondary of the H.T. transformer is earthed in the middle, and there the high-tension current passes through a shunt-type resistance of 1 ohm. The potential across this shunt is measured by means of a direct-reading potentiometer in millivolts, so if there is no leakage, the milliamperage

* Barkla and Watson, *loc. cit.*

through the tube is known. The rheostat R_1 is adjusted when necessary, so that the galvanometer in the potentiometer circuit remains undeflected: by this means the current through the tube is maintained constant within 1 per cent. The peak voltage is kept steady by employing the rheostat R_2, in conjunction with the voltmeter V, across the input to the converter, so that the reading on the voltmeter varies, under favourable circumstances, no more

Figs. 1 *a* & 1 *b*.



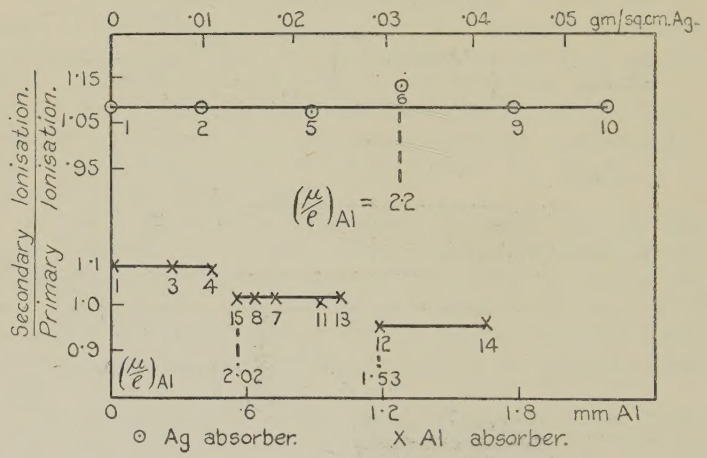
than half a volt. On account of the fact that the D.C. supply frequently falls below 230 volts, the constant reading maintained on the voltmeter is 225 volts, and this figure has been used throughout in the experiments.

2. *Experiments on the Secondary Radiation from Paraffin-Wax.*

The absorption of the secondary radiation at right angles to the exciting primary has been compared with that of the

primary by the method previously employed *. The former results with aluminium absorbing sheets have been confirmed when a plate of paraffin-wax was substituted for the cylindrical radiator, and measurements have also been made with silver and copper as absorbing materials. Equal thicknesses (x) of absorbing material were placed in the paths of the secondary and the primary beams, and the ratio of the ionizations in air was measured for different values of x. The figures 2 and 3 show the type of result obtained with Ag and Cu, compared with that with Al, measurements with absorbers of Al and Ag or Cu being made alternately.

Fig. 2.



There is a slight indication in the case of silver that the K-absorption occurs with less filtering material in the primary beam than in the secondary; this is shown by the tendency, which showed itself not only in one case, for the ratio of secondary ionization to that produced by the primary to have a slightly higher value when the mean hardness of the transmitted radiation was about that of silver K-radiation †. This is what is expected on account of the Compton effect, which causes in the scattering process a displacement of some of the energy in the spectrum

* Barkla and Watson, *loc. cit.*

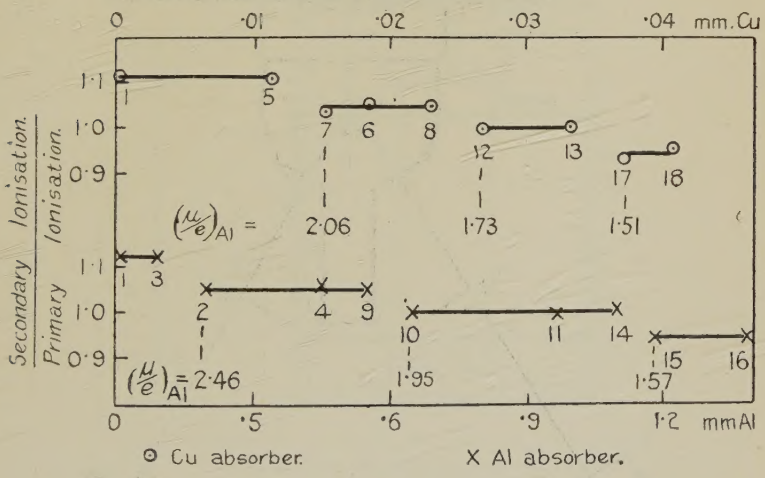
† See Barkla and Khastgir, Phil. Mag. iv. p. 735 (Oct. 1927).

of the heterogeneous beam into the longer waves. Absorption by silver in this way will not, in general, be sensitive enough to show the resulting difference in penetrating power between the primary and secondary except when the average wave-length of the heterogeneous radiation is very close to the K-absorption edge of silver.

The results for Cu and Al, on the other hand, seem to point to there being no difference in the rate of absorption of the primary and secondary beams except where the J-discontinuities occur in the secondary.

With a heterogeneous primary, a comparison of the absorption of the secondary and primary beams *over a limited thickness of absorbing material* may not necessarily be

Fig. 3.

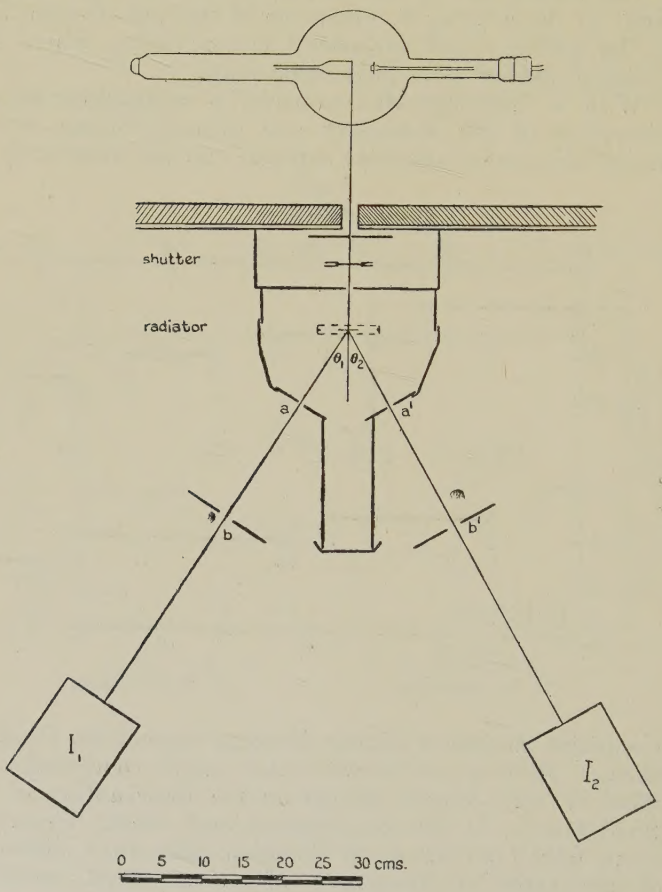


a sensitive method of testing the occurrence of the Compton effect. Factors are known which might compensate the effect of wave-length change on the absorbability of the whole beam. If the compensation were exact, the experiments would not show the Compton effect in a difference of the rates of absorption of primary and secondary radiations. It is difficult to believe that the exact compensation takes place in all these experiments so that the latter show only the occurrence of the J-phenomenon, the relation of which to the Compton effect is still obscure. This distinction of the two phenomena will be made obvious when we consider what happens when a thin fluorescent radiator is employed.

3. *Experiments with Fluorescent Radiators.*

When a thin sheet of silver or tin (about ·001 cm. say) is placed in the path of a beam of X-rays just sufficiently penetrating to excite its K-series characteristic radiation,

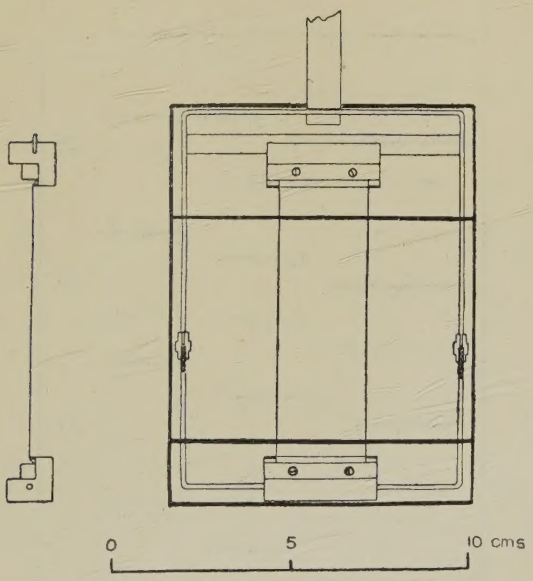
Fig. 4.



the secondary radiation contains only a small proportion (generally not more than 2 or 3 per cent.) of general radiation ; the K-series characteristic is the main secondary emission. In order to obtain in ionization measurements a sensitive means of showing J-absorption effects when material is placed in the path of the secondary beam, it is

necessary to set up two ionization chambers to receive secondary radiation in different directions from the radiator. The ratio of the ionization currents in the two chambers is then measured when equal thicknesses of material are placed in the two beams. If identical processes take place in both beams, the ratio of the ionizations should remain constant as the thickness of absorbing material is increased, and any alteration of the ratio observed will indicate differences between the two secondary beams studied.

Fig. 5.

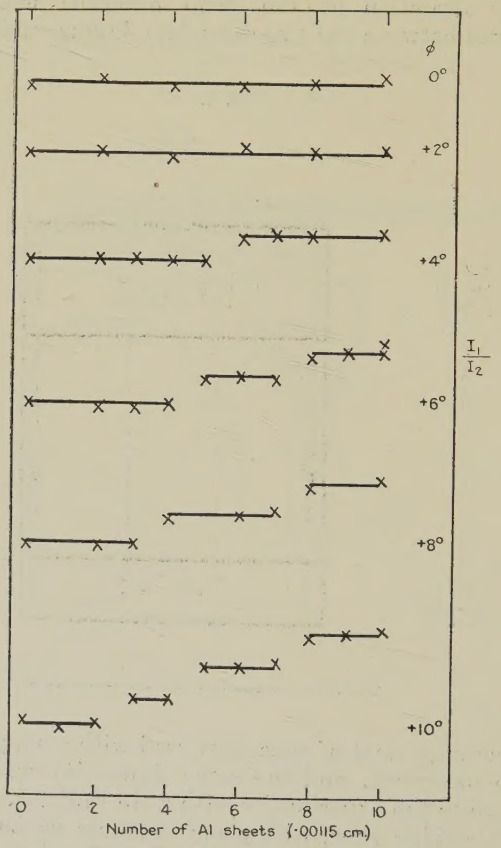


The arrangement of apparatus used with a copper radiator will be described, and the same figure (4) will serve for reference to the experiments with a tin radiator.

The Coolidge tube, with a molybdenum anticathode face set at right angles to the cathode stream, produced X-rays in a lead box ; a pencil of these passed through an adjustable vertical slit 4 cm. long and 4 mm. wide, and then encountered a lead shutter supported between brass slides 3 cm. apart. When the shutter was raised, the rays passed through a second slit to the radiator, which consisted of a sheet of copper approximately ·001 cm. thick. This sheet was stretched flat in a frame of brass (see fig. 5) protected by a

lead sheath. The frame was rigidly attached to a spindle 35 cm. long fitted axially to the vernier arm of a graduated circle, so the plane of the radiator could be set at any desired angle with respect to the direction of the primary X-ray beam. The rays which passed straight through the radiator

Fig. 6.

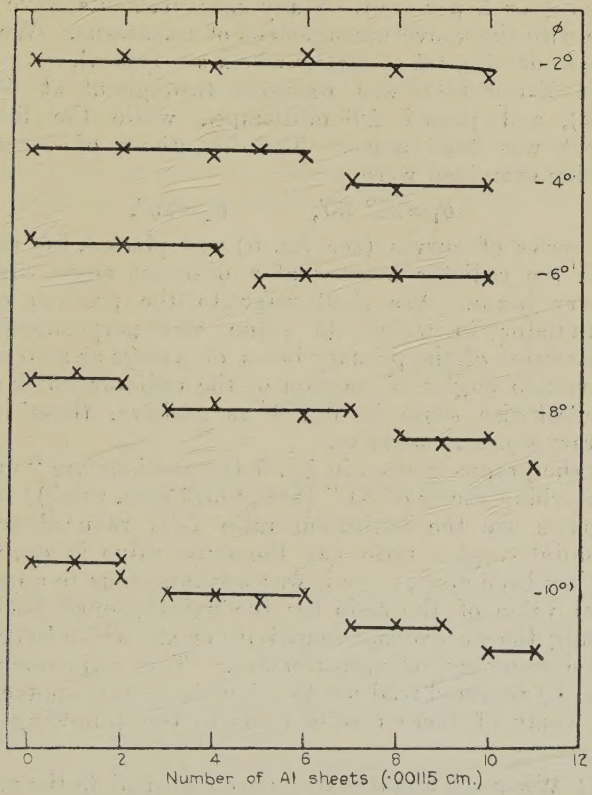


The ordinates are $\frac{I_1}{I_2}$ (reduced to same initial value 1).
The scale is obtained from the discontinuities which are on the average 7 per cent.
ϕ is the radiator angle (see text).

were trapped in a lead tunnel which was sufficiently long to eliminate stray effects due to secondary radiation from the end striking the radiator.

The secondary radiation from the copper sheet was allowed to pass, through slits a, b, and a', b', along two directions making θ_1 and θ_2 with the primary beam, to cylindrical ionization chambers containing air and provided with Al windows ·0012 cm. thick. The chambers were lined with aluminium 0·7 mm. thick and with six thicknesses

Fig. 6 (*continued*).



(For legend see p. 1152.)

of filter paper, the former to eliminate fluorescent X-rays from the walls of the chambers and the latter to prevent β-rays from the Al lining from reaching the air in the chamber. The electrodes were Al rings supporting wide mesh gauze, and sufficiently large to prevent the radiation entering the chambers from striking them; they were connected to tilted electroscopes of the Wilson type, which

were employed usually at a sensitivity of 40 divisions to the volt, and adjusted so that the deflexion of the gold leaf was sufficiently nearly linearly dependent on the leaf potential. Absorbing material was placed in equal amounts at b and b', and the ratio of ionizations was obtained by observing the deflexion in one electroscope in the period during which the shutter was raised, while the other showed a deflexion of 10 divisions. The error of reading, therefore, should not exceed 1 or 2 per cent. Many measurements have been made with the above arrangement of apparatus. We shall quote in detail a set of results which are typical.

The X-ray tube was operated throughout at 40 kv. (peak), and passed 1·8 milliamps., while the filament current was 3·52 amps. The directions of secondary emission examined were

$$\theta_1 = 24° \ 30', \qquad \theta_2 = 25°.$$

A series of curves (see fig. 6) was plotted, for each of which the radiator was set at a different angle with the primary beam. We shall refer to the position of the Cu radiator in which its plane was perpendicular to the direction of the primary beam of X-rays as zero setting and reckon angles of rotation of the radiator which are in the clockwise sense in fig. 4 as positive, those in the contrary sense as negative.

In the graphs plotted in fig. 6 the abscissæ are "number of absorbing sheets of Al" (each ·00115 cm. thick), and the ordinates are the ionization ratio I_1/I_2 reduced so that the unintercepted ratio has the same value in each case. This has been done, since it was advantageous to adjust the actual value of the ratio for the unintercepted beams by altering the electroscope sensitivity or slit width in order to ensure accuracy of measurement. This adjustment was found by repeated trial not to affect the results appreciably.

A study of these results leads to the following observations :—

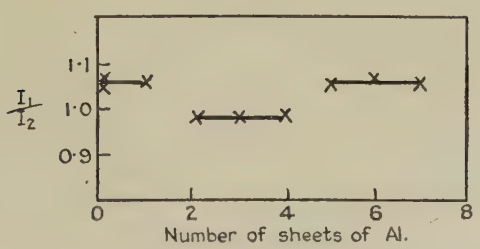
(1) When the radiator was nearly normal to the primary X-ray beam there was practically no change in the ionization ratio when increasing equal thicknesses of aluminium were placed in the beams.

(2) At other settings of the radiator the only changes in the ratio were sudden changes of about 7 per cent. When tested these were found to be due to a decrease in the ionization produced by the secondary beam which made the larger angle with the normal to the radiator.

(3) The effect of turning the radiator from zero setting in either sense was to bring one of these discontinuities gradually into the range of observation. This process was followed by making measurements at settings of the radiator intermediate between those for which the results are given in fig. 6. At greater angles a second and a third discontinuity appeared.

It may be pointed out, further, that, while the effects in the two beams seem to be separated from each other (*i. e.*, in no case in the results quoted above is there direct evidence of the appearance of discontinuities in both beams for one setting of the radiator), some other experiments have shown the simultaneous separate occurrence of two compensating discontinuities. An example of this is given in fig. 7.

Fig. 7.



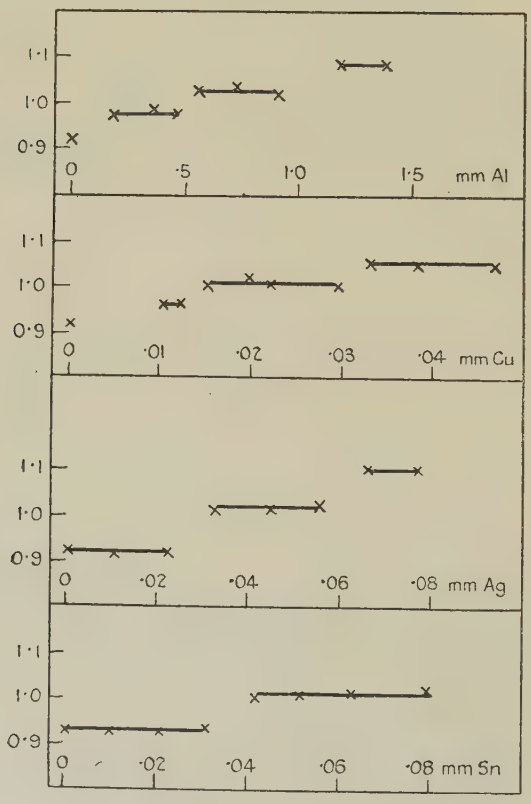
Moreover, a discontinuity may be observed when the radiator is normal to the X-ray beam, if the angle θ_1 or θ_2 is increased. It is then found, in accordance with the statement (2) above, that the ionization due to the beam making the increased angle with the normal to the radiator is reduced at the discontinuity.

In conformity with the law now well known as one of the characteristics of the J-phenomenon, the amount of absorbing material required to show a discontinuity is decreased when the peak voltage on the tube is increased.

The above measurements were made with aluminium as the most suitable absorbing substance for the soft copper K-radiation. Some other measurements, of a preliminary nature, have also been made with the secondary radiation from a sheet of tin, the absorbing substances being Al, Cu, Ag, and Sn. In fig. 8 are shown the values of the ionization ratio I_1/I_2 when equal thicknesses of absorbing material are

placed in two secondary beams ($\theta_1 = 90°$, $\theta_2 = 25°$) from a tin radiator ·00267 cm. thick. The radiator was set so that it made nearly equal angles with the two directions along which the secondary was observed. At the apertures a, a' (see fig. 4) in each beam was placed a sheet of silver about ·001 cm. thick. This acted as a filter to reduce the intensity

Fig. 8.

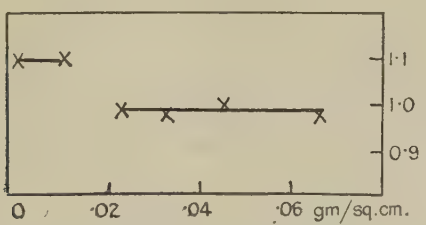


The ordinates are $\frac{I_{90}}{I_{25}}$ for Sn radiation when filtered with Al, Cu, Ag, Sn.

of the Kβ relative to the Kα component of the characteristic radiation from the tin radiator, and, on the whole, tended to reduce the amount of general radiation in the secondary beams studied. A logarithmic curve of the absorption by

aluminium gave 1·81 as a mean value of $\left(\frac{\mu}{\rho}\right)_{Al}$ for the secondary : this agrees very well with Richtmyer's value 1·78 for homogeneous radiation of the same wave-length as Sn Kα (mean of α_1 and α_2). With regard to the amount of scattered radiation present in the secondary beams, it was found that a number of sheets of paper of the same total mass per unit area as the tin radiator yielded only 1·2 per cent. of the whole secondary effect from tin. Allowing for the difference in scattering power between paper and tin, it is estimated that the secondary radiation examined must have contained not more than 4 or 5 per cent. of general scattered radiation. This estimate does not take account of the selective transparency of the silver filters which reduces the percentage of general radiation except in the case of the hardest rays, 0·2 to 0·3 Å.U. These rays,

Fig. 9.



The ordinates are $\frac{I_1}{I_2}$ for Sn radiation ($\theta_1 = 26°$, $\theta_2 = 23° 30'$) when transmitted through silver.

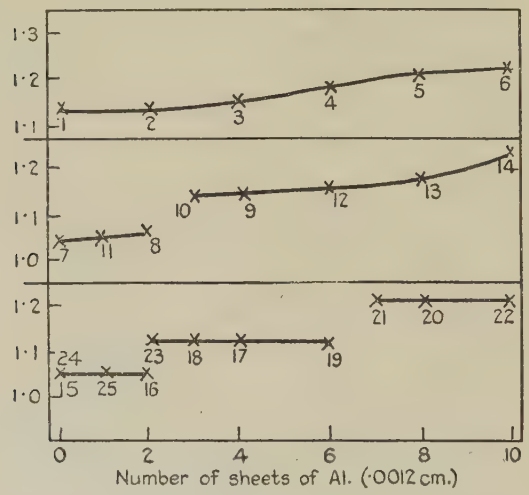
however, are less efficiently scattered by the tin radiator. We are certainly justified in concluding that the filtered radiation examined was composed of over 90 per cent. Sn Kα radiation.

Finally, fig. 9 shows a result with the secondary from tin in conditions similar to those which obtained with the copper radiator. Silver was employed as absorbing material, and the directions of secondary emission compared were $\theta_1 = 26°$ and $\theta_2 = 23° 30'$, the radiator being nearly perpendicular to the X-ray beam. It will be seen that these preliminary experiments on the secondary radiation from tin show discontinuities in the absorption by all the substances tested ; it is hoped to supplement these results by a complete investigation.

4. *Effect of Continued Running of the X-ray Tube.*

All the results quoted above were obtained only when the X-ray tube was run into a steady state. Let us now consider what happens during the establishment of that state. In fig. 10 have been plotted all the measurements of a series taken with the copper radiator and commenced just after the tube began to function. The number attached to each point denotes the order of its observation ; the time taken for the observations 1 to 6 was about 25 minutes.

Fig. 10.



Ordinates $\frac{I_1}{I_2}$ (Cu radiator).

The effects of running the tube are exhibited by the figure :—

(1) The values of the ratio I_1/I_2 are not steady until the tube has run for nearly an hour.

(2) Discontinuities appear in the relation between I_1/I_2 and the number of absorbing sheets placed in the beams.

It does not seem that the process of stabilization is accompanied by displacement of a discontinuity (*i. e.*, alteration of the amount of material required to produce it) and that the results obtained at the beginning of the series are a consequence of "smudging" due to changing conditions during

measurement, but rather it seems that, to use an analogy, the discontinuities "crystallize"—*i. e.*, they are not present until conditions are sufficiently steady. Moreover, the discontinuities occurring at greater thickness of absorbing material seem to require a longer period before they are observed.

In the attainment of a steady state a very important factor was the heating of the anticathode. It was found that stabilization was expedited by preliminary rapid heating of the anticathode, the tube being operated for 7 or 8 minutes at 60 kilovolts before the commencement of measurements at 40 kilovolts. In many cases this preliminary heating was sufficient to produce a steady state quite quickly, but in others—and in these it was noted that the tube had been idle for some days previously—it was also necessary to run at 40 kilovolts for 20 minutes before steady results were obtained.

These facts suggest that a water-cooled target should be employed and that the vacuum in the tube must be maintained steady. This latter condition may be quite easy to attain in a tube which is connected to a pump when it is operating. It is desirable, however, to attempt to introduce some such control in experiments on the J-phenomenon, and, indeed, to give serious attention to all devices to ensure steady operation of the X-ray tube.

5. *Constitution of the Beams.*

In the constitution of the beams compared we have to consider :—

(1) The ratio of the intensities of the α and β components of the characteristic K-series emission, and
(2) the intensity and character of the non-characteristic secondary radiation.

Differences between the beams with respect to (1) may be ignored, as the direct cause of detectable changes in the ionization ratio measured. Simple calculation shows that if the primary beam is changed in wave-length from that just required to excite copper K-radiation to 0·3 Å.U. (the shortest wave-length excited by 40 kv.), the ratio $I(K\alpha) : I(K\beta)$ does not alter by more than 3 per cent., and that a similar limit may be set to the variation of this ratio when the radiator is turned from zero setting through an angle $\phi \leq 10°$. This means that the difference in the relative intensity of $K\alpha$ to $K\beta$ in the beams compared cannot exceed

10 per cent. ; and even when ten sheets of aluminium (each ·0012 cm. thick) are placed in each beam the ionization ratio measured cannot be affected, in virtue of that difference, to the extent of 1 per cent.

With regard to the second factor, only strong crystal reflexion of some constituent of the primary beam into one of the directions along which the secondary is observed could produce measurable differences in the ionization ratio. The ionization due to the ordinary scattered radiation cannot, in the present experiments, exceed 1 per cent. of that due to the characteristic radiation, even when the latter has been reduced to a quarter of its original intensity by the absorbing aluminium placed in the path of the secondary beam. Consequently, the effect of absorption in the radiator on the character of this weak secondary radiation may be ignored. The calculation which determined the above figure of 1 per cent. took into account absorption of the characteristic radiation in the radiator, excess scattering in directions making angles less than 30° with the primary, and the relative ionization coefficients given by Barkla's work many years ago ; it was carried out for several wave-lengths in the primary spectrum. The shortest wave-length in the primary, of course, fixed the upper limit.

We have now to consider the effects of X-ray reflexion by the crystals of the copper sheet. On account of the rolling of the latter, it is likely that the individual crystals will not be orientated at random, and quite strong reflexion may be expected along certain directions. The lattice constant for copper is 3·61 Å.U., so that the longest waves which can be diffracted through 25° are of wave-length 1·56 Å.U. These rays are approximately of the same wave-length as Cu Kα, but in the second-order reflexion the wave-length is 0·78 Å.U., and although these harder rays are only one-tenth as efficient as the characteristic Cu radiation in producing ionization in air (and any other diffracted rays are, of course, less efficient), it must be noted that even 5 per cent. of this radiation in the secondary (intensity determined by ionization in air) will produce a 14 per cent. change in the ionization ratio measured when ·012 cm. of aluminium is placed in the beams. According to the ordinary laws of absorption the presence of secondary radiation due to crystal reflexion should show itself by making the ionization ratio change exponentially with increase in absorbing material in the path of the beams. The experimental results do not show this progressive change in the ratio, but only discontinuous changes when

definite amounts of aluminium are placed in the beams. Hence the ordinary laws of absorption fail to explain the results, whether there is strong crystal reflexion or not.

6. *The J-Phenomenon.*

The discontinuities in the ratio observed here are of the same order of magnitude as those hitherto obtained in experiments on the J-phenomenon. Moreover, in all the latter experiments, the introduction of any influence which rendered the radiation more penetrating on the whole, caused a discontinuity to appear when less absorbing material was placed in the beam. It will be noticed that the turning of the copper radiator from zero setting in the present investigation has just that effect on the secondary beam, making the larger angle with the normal to the radiator, *i. e.*, as the angle is increased the discontinuity occurs when less absorbing aluminium is placed in the beam. In addition, if the radiator is not moved and one of the angles θ_1 or θ_2 is increased, a similar effect takes place. We conclude, therefore, that fundamentally the origin of the discontinuities observed in the present investigation is very probably in the same process which determines the occurrence of the J-phenomenon.

It must be noted, however, that the absorption coefficient of the whole beam which, to a first approximation, has appeared in many experiments as one of the critical factors in determining J-absorption with heterogeneous X-radiation, is not, in the present experiments, the factor controlling the occurrence of the J-absorption discontinuities. For here, $\frac{I}{I}\frac{dI}{dx}$ is practically unchanged when a number of thin absorbing sheets is placed in the beam; the large proportion of Cu K-radiation quite outweighs the other harder secondary radiation in determining this quantity.

In the second place, while it may be that the occurrence of the discontinuities requires the presence of, at least, a small amount of hard radiation, it is quite certain that the discontinuities cannot be explained by assuming that this hard radiation itself experiences J-discontinuities, and that, on account of a sensitive state induced in the absorbing material by the J-absorption of the hard radiation, the soft characteristic radiation suffers a sudden extra absorption in passing through the specially absorbing layer. This hypothesis might explain one discontinuity : it will not explain the occurrence of two and three in a thickness of material

which scarcely affects the character of the hard secondary radiation. The experiments in which Sn K-radiation has been transmitted through silver absorbing sheets may be cited to the same effect. Thus, in general, the soft characteristic radiation itself plays a primary rôle in determining the occurrence of a discontinuity.

Thirdly, the fact that absorption coefficient is inadequate to describe the condition of the radiation from a thin fluorescent radiator, suggests that, under the conditions of former experiments, showing a series of discontinuities, the progressive change of the absorption coefficient of the whole radiation (as measured) is associated with the periodic recurrence of a condition in the radiation favourable to specially great absorption in a thin layer of absorber. This possibility suggested itself at the time of the experiments on scattered radiation in which it was shown that the absorption coefficient at the discontinuity is dependent on the current through the X-ray tube *. It was even noticed that the critical absorption coefficients formed a very approximate arithmetic series. In the present experiments it seems that a periodic variation of the conditioning factor takes place unaccompanied by a measurable change in the absorption coefficient. There is, of course, a progressive change in the relative intensity of the two characteristic components, and the possibility of greater absorption of the shorter wave component at the discontinuity. This would, of course, lead to periodic recurrence of conditions.

The conditioning factor must be latent in the emission and absorption history of the whole radiation passed through the absorber, and it will influence observable effects in a periodic way only if there is interaction between the Fourier constituents of the beam in its passage through matter. It is therefore essential to control the source of radiation very carefully, and it seems likely that experiments on the J-phenomenon which do not employ a constant source of X-radiation are not the proper experiments to investigate the phenomenon.

So far, the only mechanism that has been suggested to describe interaction between the constituents of a coherent heterogeneous beam of X-rays in its passage through matter is that X-radiation is propagated by wave-motion and that in matter the simple additive law of superposition breaks down. If the principle of the conservation of energy is to be retained, this idea encounters difficulties which have proved insurmountable in the past—it is absolutely necessary to

* Barkla and Watson, *loc. cit.*

have concentration of energy into particles in the radiation. On the other hand, Barkla * has shown, with the aid of experimental evidence, that the conception (which was already open to serious philosophical objection) of independent quantum particles corresponding to all monochromatic constituents in a heterogeneous X-radiation is untenable. It is natural, therefore, to suggest, following quantum wave-theory, that there are particles in a heterogeneous X-radiation which, in a narrow beam, are all approximately the same, but that the wave-system of each particle possesses the spectrum of the whole beam. It is possible that the remarkable features of the J-phenomenon may be suitably described in terms of a conception of this kind.

In conclusion, I have to thank Professor Barkla for suggesting that the secondary radiation from fluorescent radiators should be studied, for his interest and helpful advice and criticism throughout the work, and for the apparatus he has set at my disposal. To the Trustees of the Moray Fund of Edinburgh University I am grateful for the use of the Coolidge X-ray tube and for the high-tension batteries required for the ionization measurements.

Summary.

The ionizations produced by two secondary beams from a radiator whose K-characteristic X-radiation was excited, have been compared with equal amounts of absorbing material in the paths. Under the proper conditions of tube control, the ratio of the ionizations did not alter continuously when the amount of absorbing material (x) was increased, but exhibited discontinuities in its relation with x, which seem identical with the J-absorption discontinuities observed in former experiments.

It is shown that, except for the effects of crystal reflexion in the radiator, the radiation studied is composed almost entirely of the K-characteristic radiation of the radiator. The effect of changing the orientation of the radiator with respect to the primary beam is to displace a discontinuity, so that a different amount of absorbing material is required to produce it.

The results show that the J-phenomenon may recur periodically in absorption without appreciable change in the absorption coefficient of the beam in its passage through the absorber.

* C. G. Barkla, 'Nature' (March 27, 1926); see also Barkla & Khastgir, Phil. Mag. vol. ii. p. 656 (1926).

CXX. *Note on Modified Scattered X-Radiation and Super-Position. The J-Phenomenon* (Part VIII.). *By* Professor C. G. Barkla, *F.R.S.* *

IN previous notes it has been shown that the absorption of an X-radiation (either heterogeneous or comparatively homogeneous) and its action upon the substance in which absorption occurs depend to quite a considerable extent upon factors which had been regarded as of no significance. The properties of a heterogeneous scattered X-radiation, for instance, depend, in a very remarkable way, upon the whole atmosphere of that heterogenous beam, and not upon independent constituents.

With a certain type of radiation or sequence of radiations, it is necessary only to slightly change the average frequency of the radiation by (1) a change in the potential applied to the X-ray tube, or by (2) a change in the proportion of the various constituents such as is produced by filtering the complex radiation, or by (3) combinations in various proportions of (1) and (2), or by (4) superposing radiations of higher, or (5) of lower frequency on the beam experimented upon in order to show the sudden change in the level of its activity which we have described as the J-discontinuity †. These changes in the level of activity, dependent not upon any particular wave-length but on some kind of average measured to a first approximation by an average absorption coefficient, have been observed hundreds of times in this laboratory ; records of many typical experiments have been published.

On the other hand, there are radiations or sequences of radiations of the same average frequency which do not show this J-discontinuity ; that is, a further factor is involved which is less easily measured or even identified. All the evidence goes to show that this essential factor is some *condition* of the whole complex radiation, or sequence of radiation, as, for instance, possibly a degree of continuity or of superposition in the stream of radiation. But whatever this factor is, it is certain that the conditions showing discontinuities are separated by only a very narrow margin from those not showing such discontinuities. This critical condition then itself involves a discontinuity. Such a discon-

* Communicated by the Author.

† (4) and (5) are, of course, changes in reverse order ; (5) has been obtained in collaboration with Mr. Sen Gupta.

tinuity, produced when the average frequency (or the average absorption coefficient) remains constant, occurs

(1) in a scattered radiation with a change in the thickness (or mass) of the scattering substance ;
(2) in a scattered radiation with a change in the angle of scattering ;
(3) in a scattered radiation with a change in the frequency of interruption of the primary current in an exciting induction-coil ;
(4) in a scattered radiation (and less frequently in the primary) with some quite accidental change of an apparently trifling nature in the excitation of rays in the X-ray tube ;
(5) in the region between the state of a primary and of a scattered radiation, for a scattered radiation shows the discontinuities when the primary does not ;
(6) in a primary X-radiation when the angle it makes with the cathode stream is changed ;
(7) in a characteristic radiation from an element with some change, apparently in the primary radiation exciting it ;
(8) it also occurs in a very homogeneous beam during transmission through absorbing substances (W. H. Watson, unpublished).

All of these, then, are discontinuities of the same magnitude as the other discontinuities occurring when the average frequency (or "temperature") of the radiation remains practically constant. They are produced by a change in some other governing factor, which, so far as we can see at present, can only be identified with the large scale structure of the radiation.

The significance of two factors has, of course, been recognized from the earliest experiments on the subject. [This is in some way analogous to the manner in which the discontinuities involved in the change from the vapour to the liquid state of matter are dependent on temperature and density—within certain limits a discontinuity may be brought about by a change either of temperature or of density alone. Also the critical temperature, that is, the temperature at which the discontinuity occurs, is dependent on the density.] While there is no consistent evidence that the second factor in the case of the J-phenomenon is density (or intensity) of radiation as usually measured, there does seem to be the possibility that this is due to the fact that we can only measure an average energy density for large

volumes of radiation, while localized energy density is the important factor. Indeed, superposition definitely is of primary importance.

Confining ourselves now to a comparison of primary and scattered heterogeneous X-radiations, we can generalize by saying:—The absorbability in aluminium of the radiation scattered from very light elements in a direction perpendicular to the primary radiation is either very accurately the same as that of the primary radiation, or differs from it by a considerable amount. These are "unmodified" and "modified" scattered radiations as shown by ionization-absorption methods with heterogeneous beams. It is the step from one to the other which is the striking feature of our experimental results. We do not find such scattered radiations either more penetrating than the primary, or even slightly more absorbable—only equally absorbable, within a small possible error, or considerably and consistently more absorbable. Either of these may persist throughout experiments lasting for months; anything between is rare and transitory.

Many examples of the abrupt change from unmodified scattered radiation to a modified scattered radiation (due, that is, to a change in the level of activity) have already been given and can be multiplied. We have not, however, hitherto systematically studied the development of the modified radiation from the unmodified, except by passing the complex radiation through one of the "critical temperatures" and so observing the J-discontinuity. The following note shows the manner in which, with a suitable radiation, the modified scattered radiation may be developed from the superposition of unmodified scattered radiations. In other words, the transformation from unmodified scattered radiation is obtained, not by passing beyond a certain critical average frequency, but by changing the structure of the radiation while the same constituent frequencies are maintained in nearly the same proportion. This is a change in the second variable, which we have tentatively called the structure of the complex radiation.

When using a certain primary X-radiation excited in a Coolidge tube by an induction coil with mercury interrupter, it was found that the scattered radiation from air was an unmodified radiation, *i. e.*, a radiation with accurately the same absorbability as the primary radiation exciting it. This was shown by the fact that the ratio of the ionizations produced in two ionization chambers by the scattered and primary radiations (S/P) was precisely the same as the ratio S'/P' for the two beams when these were both intercepted by

sheets of aluminium cutting off a large proportion of the two beams. The radiation scattered from thick sheets of paper or paraffin-wax was, however, quite definitely a "modified" scattered radiation, or contained a modified radiation, *i. e.*, differed considerably in absorbability from the primary radiation. In this case S′/P′, when the intercepting aluminium was ·145 cm. thick, was 9–10 per cent. less than S/P, the ionizing effect of the scattered radiation having thus been diminished much more than that of the primary. The two radiations scattered from paper and from paraffin-wax were found to be equally modified within a small possible error. Such a result has frequently been obtained in this laboratory, *i. e.*, an unmodified scattered radiation from a gas or thin solid radiator and a modified scattered radiation from a thicker solid. In many experiments made by Mrs. Sale, for instance, the results of which are unpublished, the radiation scattered from twenty sheets of paper was an unmodified radiation, while that scattered from fifty sheets was definitely modified, as measured by these ionization-absorption methods. The result was at that time so inexplicable that we witheld it for further investigation and confined our statement of conclusions to the comparatively simple ones obtained with thin scattering sheets which yielded simple and unmistakable results *.

In our more recent experiments we made a systematic investigation of the radiation scattered from various thicknesses of scattering substance. It was found that when the sheet of paper or paraffin-wax was made gradually thinner, the difference between S/P and S′/P′, that is, the difference between scattered and primary radiations, became smaller, and ultimately almost vanished, indicating very definitely a vanishing difference for an infinitely thin layer of the scattering material.

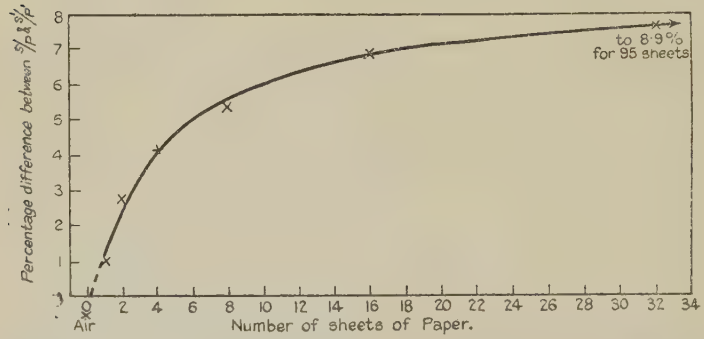
In fig. 1 a measure of the difference between the absorptions of primary and scattered radiations, or of the transformation by scattering, is plotted against the number of sheets of paper used as the scattering substance. (The radiation scattered from air had an intensity about equal to that from one sheet of paper.) The ordinate is $\left(\frac{S/P - S'/P'}{S/P}\right) \times 100$, that is, the percentage change in the ratio of ionizations produced when both beams were intercepted by ·145 cm. of Al. Thus if the magnitude of this transformation is y, the ionization produced by the intercepted scattered radiation is y per cent. less than would be the case if the scattered

* Barkla and Sale, Phil. Mag., April 1923.

radiation had been absorbed precisely like the primary. Thus from air alone the percentage of change was zero, within the possible error ; from air and one sheet of paper it was about 1·0 per cent. ; from air and two sheets of paper nearly 3 per cent. and so on approaching a definite limit of a 9 to 10 per cent. change for the radiation from thick layers of paper. The values actually obtained for y were $-0{\cdot}4$, 1·0, 2·8, 4·2, 5·4, 6·9, 7·6, and 8·9 for the radiations from air, air and 1, 2, 4, 8, 16, 32, and 95 sheets of paper respectively.

Paraffin-wax when used as the scattering substance showed precisely similar results, but equal degrees of transformation were obtained from very much greater masses of scattering paraffin. That is the curves were similar, but a much more intense radiation from paraffin was necessary to give the

Fig. 1.



same degree of transformation. Thus fig. 2 indicates the degree of modification of the scattered radiation plotted against mass per unit area (gm. per sq .cm.) of the scatterer, for both paraffin-wax and paper. (As in previous experiments, the face of the scattering slab was inclined at 45° to both primary and scattered radiations.)

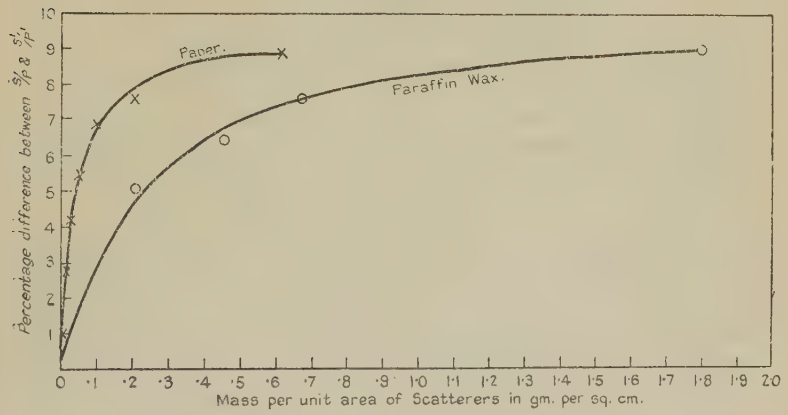
It will be seen that the maximum amount of modification was shown much earlier for a paper- than for a paraffin-wax scatterer, but the two measures of modification were finally equal—appearing as a limiting amount of modification by scattering.

The possibility of the measured difference between scattered and primary radiations being affected in some way by mere variation in the intensity of the ionization occurring in the electroscopes was quite easily disposed of by making considerable variations in the output of the Coolidge tube. Taking the most sensitive portion of the curve and using

two scattering sheets of paper, it was found that quadrupling the intensity of the radiation in this manner was entirely without influence on the measured ratio of ionizations in the two electroscopes.

But, quite independently of this, fig. 2 illustrates the same point, and perhaps much more effectively, for, as indicated, corresponding changes in the scattered radiations from paper and from paraffin-wax occurred for very different intensities of the scattered radiation, the scattered beam from paraffin-wax being seven or eight times as intense as that from paper when the same degree of modification was observed. The degree of modification appeared thus to depend upon a quality of radiation distinct from wave-length and intensity as usually measured, yet associated with superposition.

Fig. 2.



In order to study the effect of isolating the last sheet of a bundle of sheets of paper for which the scattered radiation was considerably modified, it was first observed that the modification in the radiation scattered from thirteen sheets of paper was indicated by a value of y of about 6·5 per cent. Then twelve of these sheets were moved nearer to the X-ray tube in such a position that the secondary ionization chamber and the absorbing sheets placed in the scattered beam received no radiation from them, but the primary beam still had to traverse these before falling on the thirteenth sheet. That is, the thirteenth sheet was now exposed to the same primary radiation as in the first experiment, but it alone sent secondary radiation through the absorbing sheet into the measuring electroscope. It was then found that the scattered radiation differed only very slightly from the

primary, the amount of modification being as it was in previous experiments when the other twelve sheets were completely removed. The actual figures were 0·7 and 0·9 per cent. respectively. Thus the thirteenth sheet when its radiation was examined alone emitted a radiation which was only very slightly modified; whereas this radiation, along with that from twelve other sheets, gave something approaching the full modified radiation *.

Such results were obtained for a considerable time, and were quite easily verified. It was our intention to investigate the secondary radiation further when it was in this sensitive state. After the apparatus had been left for a period of about ten days in the Easter vacation of 1927, we returned to these experiments and found that after a few experiments the unmodified radiation from air and from thin paper and paraffin-wax had been replaced by the fully modified radiation. The radiations from these substances (air, paper, and paraffin-wax) were all similar, *i. e.*, were equally modified (within the error of experiment). The critical state in which the development of the modified scattered radiation from the unmodified scattered radiation could be observed had disappeared, and we were compelled for the time to pursue other investigations †.

If any portion of such results should be regarded with greater scepticism than the other as an indication of fundamental processes, it is the modification observed with thicker layers of scattering substance, rather than the absence of modification from the thinner layer. These results, however, are not isolated; they fit consistently into a system of experimental results obtained throughout an enormous range of conditions; one result is as real as the other. Further, this degree of modification was later given by the thin sheets and even by air itself; it cannot, therefore, be attributed to disturbing effects of absorption or to any generally recognized property of radiation.

A fuller discussion can only profitably be given in a paper in which all the experimental results are summarized. This will shortly follow.

* The maximum measure of modification observed.

† We hope shortly to conduct experiments with apparatus giving a constant high tension instead of the intermittent and varying potentials applied by an induction coil or by a transformer. In the meantime, however, we have found the means for securing this critical state in another absorbing substance and have further confirmed the conclusion that the difference between the results with thin and thick radiators was not in the transmitted primary radiation, but in the different properties of the radiations scattered from these radiators.

Summary.

The results given in this note exhibit the change from "unmodified" to "modified" scattered radiations, not by passing through a certain critical average frequency as measured by an average absorption coefficient (illustrated previously by many examples of the J-discontinuity)—but by a change in the other factor involved. (See earlier papers.) In this case it was produced by the superposition of radiations of the same frequencies, and in almost exactly the same proportions. An unmodified radiation was found from air or thin paper, but the degree of modification as measured by absorption methods rapidly developed with increasing thickness of the scattering substance, and approached a limiting value.

The experiments appear to link up the classical and the quantum results, though it may be only by a combination of the two in various proportions dependent on the relative duration of two processes in the time required for an experiment.

The modification, however, depends on some kind of coherence of the whole radiation. What this means fundamentally is not yet apparent: it may, as previously suggested, depend on a certain degree of continuity or of superposition in the whole stream of radiation.

CXXI. *Cohesion and Intermolecular Repulsion.* *By* R. Kenworthy Schofield, *M.A., Ph.D., Lecturer in Physics in the University of Durham* *.

FIG. 1 represents diagramatically the variation of the mutual force with distance for the rigid-sphere type of molecule postulated by numerous theorists. These molecules are regarded as spherical, and the force is an attractive one which increases steadily as their centres approach one another. The curve ends abruptly at a distance equal to twice the molecular radius, since the molecules, being supposed absolutely rigid, cannot be closer than this.

Fig. 2 similarly represents the force between two molecules whose fields are of the complex type postulated many years ago by Young and Rayleigh, and recently subjected to mathematical treatment by Lennard-Jones [1]. Here also, for the sake of simplicity, the field is regarded as having spherical symmetry with respect to a centre. In this case, as the

* Communicated by Prof. J. E. P. Wagstaff, D.Sc.

centres approach one another, the mutual attraction increases to a maximum, falls to zero, and then changes to a repulsion which increases very rapidly.

In a liquid or compressed gas, consisting of molecules of the rigid-sphere type, the cohesion would increase continuously with reduction in volume. With molecules of the complex-field type, however, the cohesion might be expected to rise to a maximum, and then become less with further reduction in volume. With this idea in mind, the author calculated the cohesion in a number of gases and liquids at a series of volumes from the data of Amagat [2]. The interest

Fig. 1.

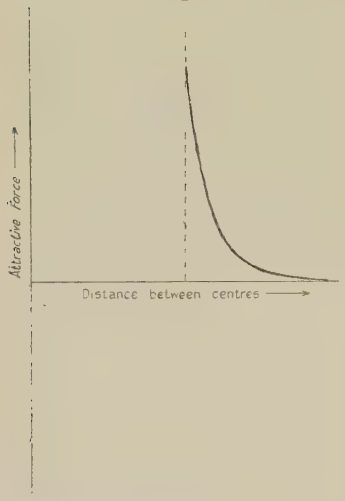
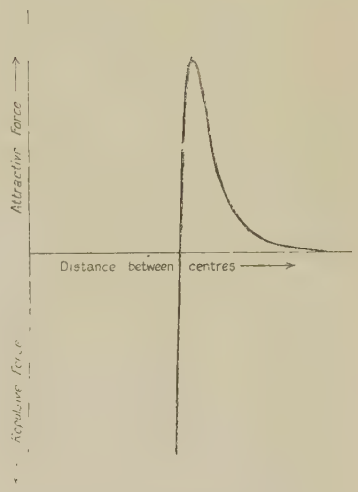


Fig. 2.



of the results obtained seems sufficient to warrant their publication.

Determination of Cohesion.

As there is no universally accepted method for evaluating cohesion, it is necessary to explain and, it is hoped, justify the one used.

The heat dQ, taken up by a fluid during a reversible expansion dv, goes partly to the performance of external work pdv, against the external pressure p, and partly to increasing the internal energy U. Thus

$$dQ = \left(\frac{dU}{dv}\right)_T dv + pdv.$$

But, by the Clapeyron-Claussius relation,

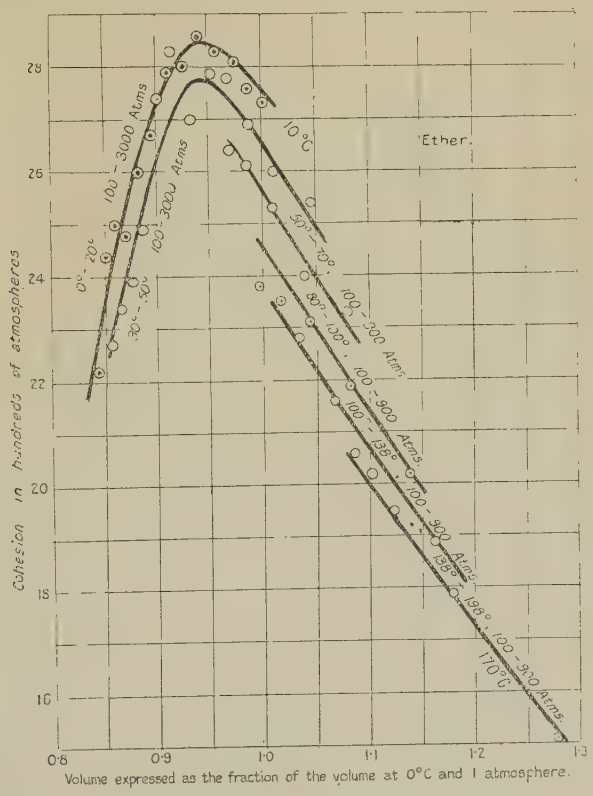
$$dQ = T\left(\frac{dp}{dT}\right)_v dv.$$

Hence

$$\left(\frac{dU}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v - p,$$

a well-known thermodynamic relation.

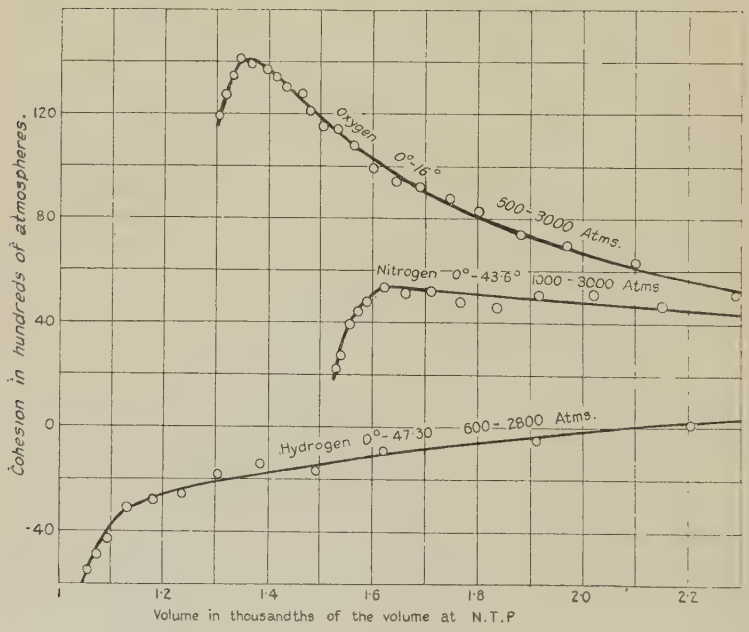
Fig. 3.



$(dU/dv)_T$ has the dimensions of a pressure. In forming an idea of its significance, it is necessary to distinguish between the case where molecular encounters sometimes lead to temporary chemical union, and the case where this does not occur. The possibility of chemical union is not taken account of in either of the molecular theories under consideration. Hence discussion of the case where chemical

unions occur is not germane to the present inquiry. Where no chemical unions occur, the number of molecules (*i. e.* the number of entities taking part in thermal agitation) will not be affected by a change in volume. Hence an isothermal expansion dv will not affect the total translational kinetic energy (the K. E. associated with the movements of the centres of mass of the molecules), and so the increase in internal energy $(dU/dv)_T dv$ is the direct outcome of the mutual separation of the molecules consequent upon the expansion. Thus $(dU/dv)_T dv$ is the energy that must be

Fig. 4.



supplied in order to effect the necessary separation of the molecules, and therefore it seems reasonable to give the name cohesion to $(dU/dv)_T$. In using this word, no restriction upon the form taken by the ingoing energy is implied, except that it is not chemical and not translational kinetic.

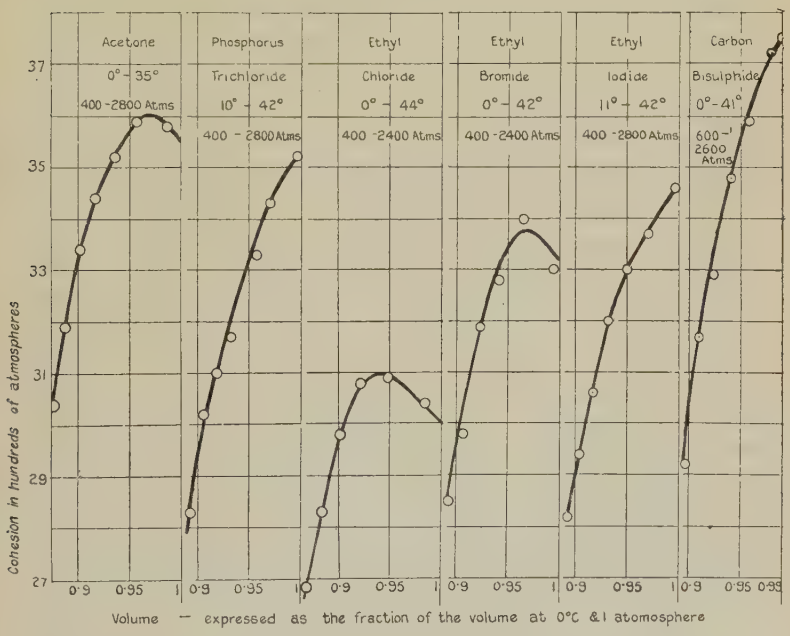
Discussion of the Curves.

Curves showing the variation of cohesion with volume are given in figs. 3, 4, and 5. These cover all the substances investigated by Amagat, with the exception of water and

four alcohols which have been excluded because molecules of these substances are believed to associate chemically. The most striking feature of the curves for the remaining substances is the final decrease in cohesion with decrease in volume which occurs in every case—this gives emphatic support to the complex-field, as opposed to the rigid-sphere theory.

The curves * for ether form a link between the oxygen curve and those for the liquids. They are also important in showing that, for this substance, the cohesion at a given

Fig. 5.



volume decreases with temperature (over the volume and temperature range of Amagat's experiments) †. The data

* It was found best to obtain $(dp/d\mathrm{T})_v$ as the product of $(dv/d\mathrm{T})_p$ and $-(dp/dv)_\mathrm{T}$ calculated from Amagat's figures for the volumes at two neighbouring temperatures and at a series of pressures. These two temperatures are stated for each curve; the cohesion will presumably be that for the mean temperature. A certain amount of straying of the points from the smooth curve is to be expected, especially when the two temperatures are not very different.

† There is evidence from the data of Young[3] that, at rather larger volumes (*i. e.* just less than the critical volume) and at higher temperatures, the cohesion increases with temperature.

for the three gases only permit of determination of the sign of the temperature variation of the cohesion as far as $p = 1000$ atmospheres ($v =$ about 18), but thus far it is the same in all three cases as for ether. It is possible, therefore, that the curves for oxygen, nitrogen, and hydrogen are typical of the stages through which the curves for the other substances would pass at sufficiently high temperatures.

The quantitative interpretation of the cohesion in terms of the forces between individual molecules is obviously an exceedingly complex problem in statistical mechanics, seeing that the relative position of the molecules is constantly changing on account of their thermal movements. Yet it will be seen in a general way that the more violent the thermal agitation, the more deeply will the molecules (considered to be of the complex field type) penetrate into the inner (repulsive) parts of each other's fields. Thus the ratio of the time that molecules repel each other to the time that they attract each other increases with the temperature. This may account for the temperature variation of the cohesion, and its negative value in hydrogen at 24° C.

In conclusion, I gladly take this opportunity of expressing my gratitude to Professor Masson for the interest he has taken in this work and for several very helpful suggestions.

Summary.

The cohesion in a number of highly compressed liquids and gases has been calculated over a wide pressure range. As the volume is reduced the cohesion first increases to a maximum and then decreases.

The results cannot be reconciled with the view that molecules resemble rigid spheres, but are readily accounted for on the view that the force between two molecules is repulsive when they are very near together, and attractive when they are further apart.

References.

(1) Lennard-Jones, Proc. Roy. Soc. A. cvi. p. 463 (1924), & cxii. p. 214 (1926). Faraday Soc. Trans. xxiv, p. 100 (1928).

(2) Amagat, *Annales de Chimie et de Physique*, series 6, p. 29 (1893).

(3) Young, Phil. Mag. 5, xxiii. p. 435 (1887); Proc. Phys. Soc. xiii. p. 602 (1895); Phil. Mag. p. 47 (1899).

CXXII. *The Velocity of Sound in Liquids at High Frequencies by the Sonic Interferometer.* *By* Prof. J. C. Hubbard (Johns Hopkins Un.) *and* A. L. Loomis. (Communication No. 3 from the Loomis Laboratory, Tuxedo Park, N.Y.) *

Introduction.

THE method of measuring the velocity of sound in liquids herein described, has been developed for the purpose of securing results of high precision with the employment of relatively minute quantities of liquid. From the results it is possible to deduce the adiabatic compressibility, and when the specific heat at constant pressure is known, the isothermal compressibility, difference of specific heats, increase of internal energy with volume at constant temperature, and so forth. The method is, therefore, capable of furnishing information of thermodynamic importance. The precision attainable is such that the instrument promises, like the refractometer or pycnometer, to be of use to physicists and chemists for empirical analysis.

The measurement of the velocity of sound in liquids by methods hitherto used is beset with peculiar difficulties, either of experiment or of interpretation. The velocity is of such magnitude that the direct method necessarily has been restricted in application to large bodies of water. Most painstaking effort has been expended in securing data on salinity and temperature with the object of specifying these quantities for the velocity found. Resonance methods at audible frequencies have been tried by a number of observers. Such methods call for large-size apparatus and a large quantity of liquid, restricting measurements to commoner and more easily purified substances. These methods, moreover, involve a serious correction factor owing to the influence of the materials and dimensions of the apparatus upon the wave-length. The interesting experiments of Dörsing † and others, using resonance methods, have yielded a large number of values of the velocity of sound in different liquids, in most cases for temperatures between 15° and 20° C. Owing to the different correction formulæ used and to different means of approximation

* Communicated by Prof. R. W. Wood.

† K. Dörsing, *Ann. d. Phys.*, xxv. pp. 227–251 (1908). See also *Handbuch der Physik*, viii. Akustik, p. 641; W. Busse, *Ann. d. Phys.* lxxv. pp. 657–664 (1924).

employed by various observers, the results, where comparable, are in serious disagreement. The latest and probably the best of the experiments by the resonance method at audible frequencies are those by Pooler *, who has measured the velocity of sound in distilled water as a function of the temperature. He has made use of a correction formula developed for special application to his experiments by Gronwall †.

Langevin made use of the piezoelectric property of quartz for the purpose of generating a beam of high-frequency sound-waves for the detection of submarines. Wood and Loomis ‡ have made an extensive study of the effects of such waves and have described a number of phenomena depending upon standing wave systems produced in a vessel of oil containing a quartz plate driven at high frequencies. They were able to estimate the half wave-length in oil by the observation of a number of effects, and the work of the present paper makes use of these experiments as the starting point.

Boyle § has published a series of studies of beams of sound-waves produced by a piezoelectric plate in a large tank. He has produced standing wave systems in water and in castor oil, and gives the velocity of sound in these liquids at a number of frequencies. These values are significant within one per cent, but are restricted to the neighbourhood of a single temperature. Boyle does not find any sensible dependence of velocity upon frequency within the range of his experiments.

Preliminary results by the method described in the present paper have been published by the authors ‖. The present paper summarizes all the results of value obtained at the Loomis Laboratory, Tuxedo Park, during the summer of 1927.

Apparatus and Method.

The sonic interferometer for liquids consists of a cylindrical chamber containing the liquid to be studied, in which plane compressional waves are produced by a piezoelectric

* L. G. Pooler, Phys. Rev. xxxi. pp. 157–158 (1928) (Abstract).

† T. H. Gronwall, Phys. Rev. xxx. pp. 71–83 (1927).

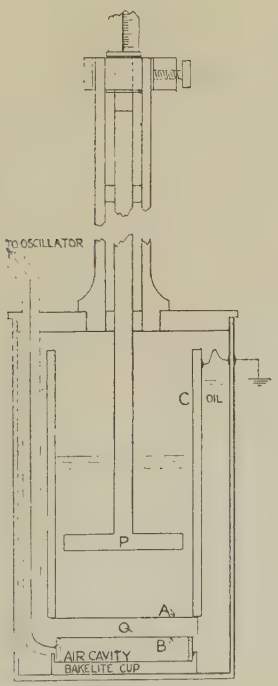
‡ R. W. Wood and Alfred L. Loomis, Phil. Mag. iv. pp. 417–436 (1927). See also W. T. Richards and A. L. Loomis, Journ. Am. Chem. Soc. xlix. pp. 3086–3099 (1927).

§ R. W. Boyle, Trans. Roy. Soc. Can. iii. p. 141 (1923); pp. 159, 191, 197 (1925); p. 79 (1927). See also 'Nature,' cxx. p. 476, Oct. 1 (1927).

‖ J. C. Hubbard and A. L. Loomis, 'Nature,' cxx. p. 189, Aug. 6 (1927); Phys. Rev. xxxi. p. 158 (1928) (Abstract).

plate maintained in forced vibration by connexion of one of its electrodes with a point on the coil of a high-frequency oscillating electrical circuit, the other electrode of the plate being in contact with the liquid and grounded. The waves are reflected by a movable piston, which may be displaced by a micrometer screw so as to be set at successive positions for the production of standing waves. The frequency of oscillation is so high that the wave-length in the liquid is

Fig. 1.



short in comparison with the diameter of the plate. (We have used quartz plates of 50 mm. diameter, the wave-length in the liquid being in the neighbourhood of 3 mm.) Under these conditions our experiments have shown that the effect of the walls of the vessel may be entirely neglected when the piston is within a few cm. of the plate.

In fig. 1, let Q be the quartz plate, A and B the electrodes, the latter connected to the coil of the oscillating electrical system and the former closing the end of the cylinder and

serving as a diaphragm for the transmission of the vibrations of the quartz plate to the liquid. The diaphragm A as well as the cell C and the piston P are all grounded. In the experiments about to be recorded, the results for water and for salt solutions were obtained with instruments exactly as here described, except that an outer chamber filled with oil was provided to serve as a temperature bath. All parts exposed to the liquid being studied were gold-plated. In the experiments with mercury the cell C consisted of a small pyrex beaker, the bottom of which was ground plane inside and out. The beaker rested upon a thin foil serving as the grounded electrode on the upper side of the quartz. The piston in this case was cut from the bottom of a pyrex beaker and fused to a pyrex rod, the piston afterwards being ground plane. Owing to the fact that part of the piston rod is in an unhomogeneous temperature field when working with temperatures in the liquid chamber far from that of the room, the rod should have a small coefficient of expansion. The rods used with all substances except mercury were of quartz or of invar. The piston is displaced vertically by a Brown and Sharp micrometer screw, the head of which is divided into hundredths of a millimetre. Since the results reported in this paper were obtained, great improvements have been made in the design of the interferometer, so as to prevent loss of vapour of the liquid and to render the instrument suitable for deep immersion in a thermostat or in a Dewar flask. The various forms of instruments which we have devised will be the subject of a paper which will appear in another place. It remains to be said that the one requirement for successful operation is that there be no air or gas bubbles between the quartz plate and the liquid in which it is desired to produce waves. Mechanical coupling between the quartz and the liquid is secured by the use of a transformer oil, a few drops being placed upon the quartz plate before it is put in contact with the diaphragm. Similarly in case a glass vessel is to replace the cell C, there must be an oil film between the plane bottom of the vessel and the electrode.

The electrical circuit which is used to drive the quartz plate is of the usual type of oscillator; it is provided with a variable condenser, and the frequency is adjusted so as to be somewhat removed from the natural frequency of the quartz plate in order to avoid distortion of wave-form. In nearly all the experiments recorded here a vernier condenser was also provided for a purpose that will appear below.

As the piston is displaced through the liquid, the tuning of the liquid column varies, passing through successive resonance points. The impedance of the liquid varies through a cycle, causing a corresponding variation in the reaction of the liquid on the quartz plate, and through the inverse piezoelectric effect a corresponding reaction is produced in the electrical circuit. This variation produces a number of effects, any one of which may be used as a basis of measurement of the half wave-length of the compressional wave in the liquid. Among these cyclic variations are : plate current of oscillator observed by means of a milliammeter; voltage variation in the coil, measured by voltage amplifier (designed for us by Dr. A. W. Hull) ; voltage variation in the coil indicated by a neon lamp, so placed as to be extinguished at the instant of passage through resonance ; variation in frequency of oscillation which may be detected by the cyclic changes of reading of the milliammeter of a wave-meter which is loosely coupled to the oscillator; variation of heterodyne beat with a second oscillator of constant frequency ; variation in current in high-tension lead to the quartz plate indicated by vacuum thermocouple and galvanometer. For the purpose of most precise measurement and by means of which all the results here reported were measured, we have used a double heterodyne method, similar in principle to that used by Whiddington in his "ultra-micrometer." By this method the frequency is automatically held constant and the half wave-length to be determined is thus invariable.

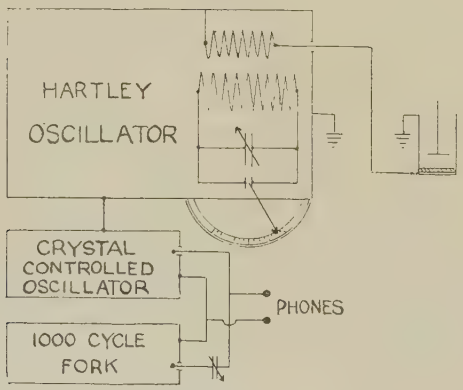
The main oscillator (fig. 2) is loosely coupled to a crystal-controlled oscillator of known frequency. The heterodyne beat note thus produced is then tuned by means of a vernier condenser to unison with a tuning fork, the frequency of which is 1000 cycles per second. The frequency of oscillation of the main oscillator and thus of the interferometer plate is accordingly that of the piezoelectric oscillator, plus or minus 1000 cycles per second.

In some of the experiments we have used, in the crystal-controlled oscillator, a crystal ground to 501,000 cycles $\pm$ 0·01 per cent., so that with a beat note of 1000 cycles the main oscillator is kept at exactly 500,000 cycles. As a result, the velocity of sound in metres per second has the same numerical value as the half wave-length in the liquid in thousands of a millimetre, and accordingly may be read directly from the screw.

As the piston is advanced through the liquid column, the reaction on the main oscillator is such as to require a cyclic

variation of the vernier condenser in order to maintain unison of the heterodyne note with the fork. If we plot vernier condenser readings as ordinates and screw readings as abscissæ we may take as the half wave-length in the liquid the difference in screw readings corresponding to two adjacent similar mean points on the curve. In practice, the reaction is so sharp at the node that settings may be made by ear within a few thousandths of a millimetre. Usually we have determined the position of three successive settings nearest the diaphragm, then of three successive positions about 2 cm. beyond. Under usual conditions the precision obtainable in the value of the half wave-length

Fig. 2.



from such readings is about one part in five thousand. The following illustrate the magnitudes of quantities involved and the variations in their measurement.

Mercury. $t=20°{\cdot}0$ C.

Setting.	Screw, cm.	Difference.	Setting.	Screw, cm.	Difference.
1	·4445		12	2·2695	
2	·6105	·1660	13	2·4368	·1673
3	·7772	·1667	14	2·6034	·1666
Mean ...	·6107		Mean ...	2·4366	

Displacement for 11 half wave-lengths, 1·8259 cm.
$\lambda/2=·16582$ cm. $f=437{,}600$ cycles/sec.
$u=1451{\cdot}3$ metres/sec.

The following results, from similar measurements, include all those found for mercury at 20·0° C.:—

$\lambda/2$, cm.	u, m./sec.
·16579	1451·0
·16576	1450·7
·16570	1450·2
·16580	1451·1
·16583	1451·4
·16580	1451·1
·16582	1451·3

Mean $u = 1451{\cdot}0$ m./sec. Average deviation, $\pm 0{\cdot}3$ m./sec.

Thermodynamic Relationships.

The velocity of sound in a liquid is given by

$$u = (1/\beta_\phi \rho)^{\frac{1}{2}} = (k/\beta_T \rho)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (1)$$

where β_ϕ and β_T are respectively the adiabatic and isothermal compressibilities of the liquid, ρ is the density, and k the ratio of specific heats, c_p/c_v. Using the relations

$$c_p - c_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial v}{\partial p}\right)_T \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p; \quad \beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T, \quad . \quad (3 \& 4)$$

we have

$$c_p - c_v = T\alpha^2/\beta_T \rho = T\alpha^2 u^2/k \quad . \quad . \quad . \quad . \quad (5)$$

and

$$k = 1 + T\alpha^2 u^2/c_p. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For purposes of calculation it is more convenient to use, in place of α, the quantity $\alpha_0 = (\partial v/\partial T)_p/v_0$, which may be found for a number of substances from data in standard tables. Equations (5) and (6) then take the form

$$c_p - c_v = \frac{T\alpha_0^2 u^2}{k} \cdot \frac{\rho^2}{\rho_0^2} \quad . \quad . \quad . \quad . \quad . \quad (5')$$

and

$$k = 1 + \frac{T\alpha_0^2 u^2}{c_p} \cdot \frac{\rho^2}{\rho_0^2}. \quad . \quad . \quad . \quad (6')$$

From (6′) it is thus possible to calculate the ratio of specific heats of a liquid for which the specific heat at constant pressure is known. Since in most cases α_0, ρ, and ρ_0, and, as it is hoped the present paper will show, u, may be deter-

mined to a high order of accuracy, the computed value of k is limited in precision at present only by the limitations of existing data on c_p.

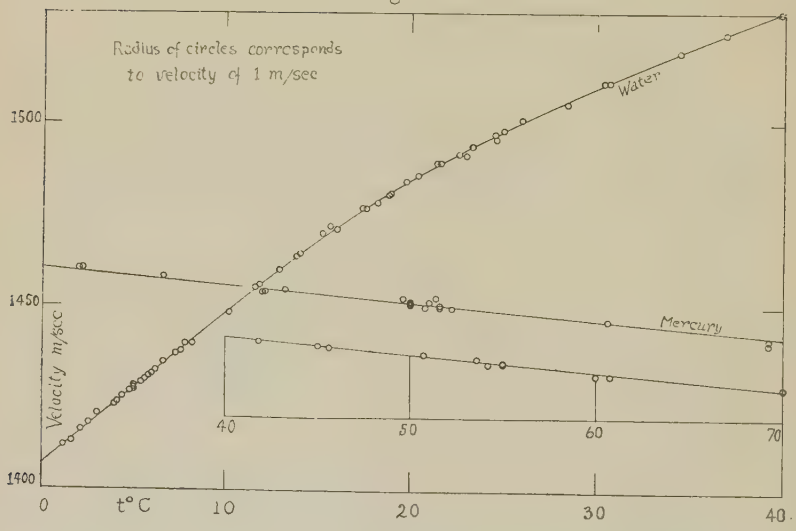
Having determined k, $c_p - c_v$ may be found from (5′). Other coefficients of especial interest are:

$$\left(\frac{\partial v}{\partial p}\right)_T = \frac{k}{u^2\rho^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$\left(\frac{\partial E}{\partial v}\right)_T = \frac{\rho_0}{\alpha_0}(c_p - c_v) - x \quad . \quad . \quad . \quad (8)$$

Fig 3



Results.

The velocity of sound has been measured in the manner described for water from zero to 40° C.; for mercury from zero to 70° C.; for five solutions of NaCl; two of NaI; and one of KCl. Data were obtained for CS_2, chloroform, toluene, and acetone, which were of use in suggesting improvements in the design of the instrument, especially in respect of insuring against liability to absorption of water-vapour from the atmosphere; but these data are not included here, as contamination was quite possible with the instrument as used.

Fig. 3 represents in graphic form the results for water and for mercury. The points on the water-curve were

obtained with three different instruments, using a four-fold variation in wall-thickness of measuring vessel, a number of different modes of attachment of diaphragm, and both with and without a surrounding oil-bath for temperature control. The oil-bath, when used, was immersed in a larger water thermostat. The intensity of the electrical vibration was varied from that which produced a barely perceptible heating effect to a value so small that it was just possible to detect nodes. It was found that a most gratifyingly large margin for use in measurements exists in the power which may be employed between the value which will produce sensible error due to heating and the smallest value that will permit a precise definition of nodes. The procedure has been to draw a smooth curve through the points, and from the smooth curve to read off values at intervals of 5° for computation of thermodynamic quantities. Table I. presents these quantities for water.

TABLE I.—Water.

$t°$ C.	u, m./sec.	k.	$c_p - c_v$ $\frac{\text{cal.}}{\text{gr. deg.}}$	$\left(\frac{\partial v}{\partial p}\right)_T \times 10^{10}$.	$\left(\frac{\partial E}{\partial v}\right)_T 10^{-7}$.
0 ...	1407·0	1·0005847	·0005872	·5056	−36·53
5 ...	1427·7	1·00003438	·00003448	·4906	+ 8·943
10 ...	1448·8	1·001086	·001086	·4772	51·82
15 ...	1467·5	1·003357	·003345	·4667	92·86
20 ...	1484·2	1·006556	·006506	·4586	131·82
25 ...	1498·1	1·010583	·010454	·4529	169·6
30 ...	1509·9	1·01525	·01499	·4492	205·6
35 ...	1520·6	1·02037	·01992	·4466	239·7
40 ...	1530·3	1·02575	·02505	·4449	271·5

The coefficients of expansion of water are calculated from the formulæ of Chappuis. The values of c_p are taken from 'Handbuch der Physik,' x. p. 323.

It is interesting to compare the value for $c_p - c_v$, ·0079 at 22° and zero pressure obtained by Bridgman * for water, with the value ·008004, calculated from the velocity of sound, $u = 1490{\cdot}2$ m./sec. at 22°. F. A. Schulze † gives for $c_p - c_v$ the values ·0005 and ·006 respectively at 0° and 20° C. The other quantities are in similar agreement with published data. It will be observed, however, that the values recorded

* P. W. Bridgman, Proc. Am. Acad. of Arts & Sciences, xlvii. p. 549 (1912).

† F. A. Schulze, *Phys. Zs.* xxvi. p. 155 (1925).

in the present paper may be regarded, in the case of quantities proportional to $c_p - c_v$, as having four significant figures, and that the decimal part of k also has four significant figures.

Corresponding data for mercury are given in Table II.

Table II.—Mercury.

$t°$ C.	u, m./sec.	k.	$c_p - c_v$ $\frac{\text{cal.}}{\text{gr. deg.}}$	$\left(\frac{\partial v}{\partial p}\right)_T \times 10^{12}$.	$\left(\frac{\partial E}{\partial v}\right)_T \times 10^{-7}$.
0 ...	1460·2	1·1371	·004034	·2885	1264
10 ...	1455·6	1·1415	·004132	·2925	1294
20 ...	1451·0	1·1457	·004228	·2965	1322
30 ...	1446·4	1·1499	·004322	·3006	1350
40 ...	1441·7	1·1539	·004412	·3047	1377
50 ...	1437·1	1·1579	·004501	·3089	1404
60 ...	1432·4	1·1618	·004587	·3131	1429
70 ...	1427·7	1·1655	·004670	·3173	1454

Bridgman* gives ·0544 gram calories for the difference $c_p - c_v$ for 13·596 grams of mercury at 0° C. From the above table we obtain, for comparison, $\cdot004034 \times 13\cdot596 = \cdot05484$. Bridgman gives values of $\left(\frac{\partial v}{\partial p}\right)_T$, which in c.g.s. units reduce to $\cdot286 \times 10^{-12}$ and $\cdot297 \times 10^{-12}$ for 0° and 22° respectively, as compared with $\cdot2885 \times 10^{-12}$ and $\cdot2973 \times 10^{-12}$ obtained from the above results for the same respective temperatures. The value of k for mercury at 0° C. is frequently taken to be 1·14 (see, for example, Planck, 'Thermodynamik'). So far as we can find, there is no previous record of any measurements of the velocity of sound in mercury.

One phenomenon of marked interest was observed in the measurements with mercury. If the power supplied by the oscillating circuit is not reduced greatly below any value at which heating of the mercury can be observed, the indication of resonance is at once destroyed. That is, as the piston advances through the mercury, a resonance-point is reached, only to disappear immediately, no further movement of the piston indicating a resonance-point for some seconds. It seems probable that, in view of the very high absorption

* P. W. Bridgman, Proc. Am. Acad. Arts & Sciences, xlvii. p. 383 (1911).

observed by Wood and Loomis (*loc. cit.*) for high-frequency waves in mercury, we may expect a heating at nodes causing a heterogeneity of the medium and destroying the plane-wave system. To guard against this phenomenon, the amplitude of oscillation was reduced until the heterodyne beat note, the vernier condenser being unchanged, varied by not more than ten or twelve vibrations per second from the pitch of the fork as the piston was advanced from node to node. A second difficulty in these measurements with mercury arose from the fact that, owing to the improvised nature of the glass cell in which the measurements were made, the vibrating quartz plate was separated from the mercury by a glass wall which was not accurately plane-parallel, and which had several visible flaws in it. Probably, owing to this cause, some of the measurements deviate more widely than is the case with any other substance which we have tried. All the points obtained are shown in fig. 3.

Five solutions of sodium chloride were studied. Table III. presents the values of the velocity of sound obtained. The concentration is expressed in weight per cent. NaCl. The values given for the three solutions of lower concentration are reduced from the values reported by the authors in 'Nature,' it being found that, owing to a curvature of the carriage-guides carrying the piston-support used in those measurements, the results were all too high by approximately 0·6 per cent.

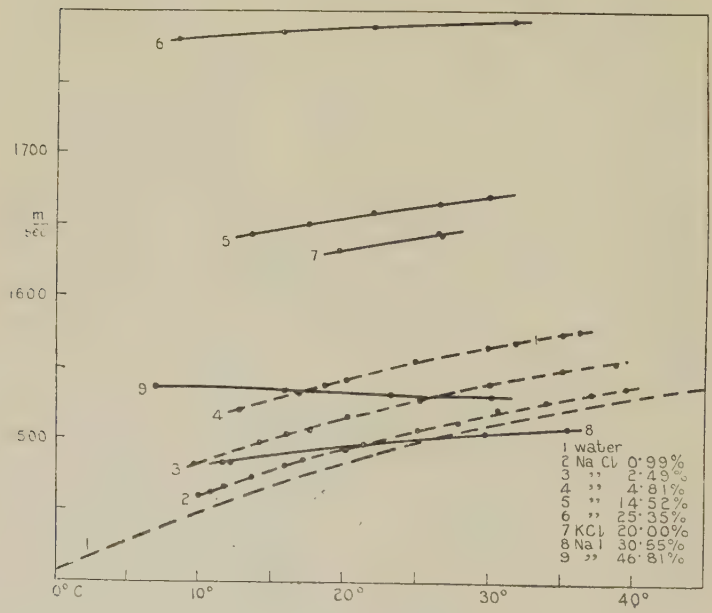
TABLE III.—NaCl Solutions.

	·99 per cent. NaCl.	2·49 per cent. NaCl.	4·81 per cent. NaCl.
$t°$ C.	u, m./sec.	u, m./sec.	u, m./sec.
10	1460	1483	
20	1492	1515	1542
30	1517	1538	1565
40	1538	1556	1583

14·52 per cent. NaCl.		25·35 per cent. NaCl.	
° C.	u, m./sec.	$t°$ C.	u, m./sec.
13·8	1644·1	8·25	1780·2
17·6	1650·9	15·8	1786·0
22·0	1658·5	22·05	1789·3
26·7	1665·6	31·8	1792·9
29·2	1669·4	31·95	1792·9

Smooth curves have been drawn through the points plotted, u being ordinates and t abscissæ. These are indicated in fig. 4, curves 2, 3, 4, 5, and 6. To show the effect of concentration of the salt upon the velocity of sound, the values of u have been taken from large-scale plots at the respective temperatures of 16° and 30° C. Fig. 5 shows u as a function of the weight per cent. of NaCl. It is interesting to note that the values of the velocity of sound in NaCl solutions at a given temperature are almost exactly linear

Fig. 4.



with the percentage of salt. We have chosen the value of $t=16°$ C. for comparison with the data summarized in the 'Handbuch der Physik,' vol. viii. p. 642. The curves there shown are reproduced as curves B, D, and V in fig. 5. Curve B is computed from measurements of O. Tait (1889) on the compressibility of salt solutions. Curve D shows three points obtained for the velocity of sound in salt solutions at 16° C. by Dörsing (1907). Curve V shows values of u obtained at the same temperature by Veenekamp (1922). The Handbuch should be consulted for additional

discussion of these values. Our measurements indicate a slight departure from linearity with concentration, but do not indicate any obvious effect of dissociation.

Table IV. gives the results for the one solution of KCl which was studied. This case shows a marked similarity to that of NaCl in the same region of velocities (fig. 4, curve 7).

Fig. 5.

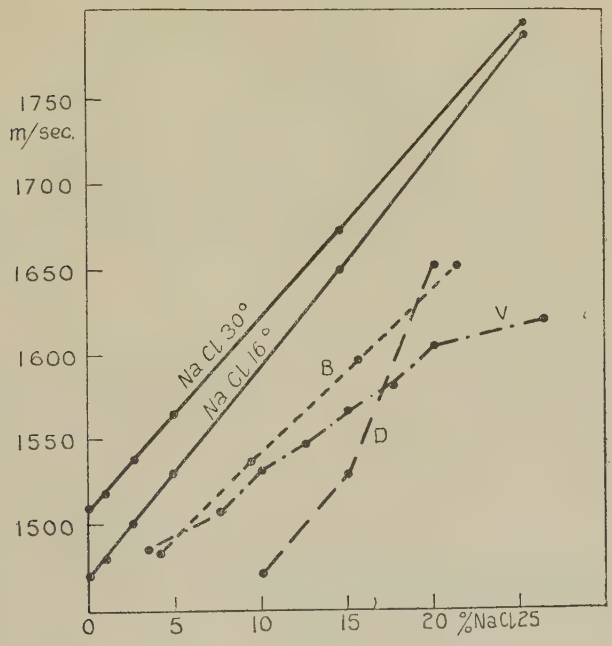


TABLE IV.

KCl, 20·00 per cent.: Water, 80·00 per cent.

t.	*u*, m./sec.
19·8	1632·5
26·6	1643·4
26·7	1643·7

Table V. shows the values of *u* which have been found for two solutions of NaI in water.

TABLE V.

30·55 per cent. NaI.		46·81 per cent. NaI.	
t.	*u*, m./sec.	*t.*	*u*, m./sec.
11·6	1484·3	7·0	1536·3
12·2	1484·5	16·0	1534·5
21·5	1497·0	23·4	1531·9
29·9	1503·8	30·4	1530·8
35·5	1508·9		

These values are shown in fig. 4, curves 8 and 9. These solutions are of especial interest, showing above 25° C. an actual decrease in the velocity of sound as compared with pure water for moderate concentrations, and an increase to values greater than for pure water at higher concentrations. Mr. E. B. Freyer, working at Johns Hopkins University with one of the authors, has confirmed these results, and has observed a similar behaviour for solutions of potassium iodide.

Summary.

In the foregoing paper is described a new method of measuring the velocity of sound in liquids at high frequencies. A circular plate of quartz two inches in diameter, with plane-parallel faces, is caused to vibrate piezoelectrically at such frequencies that the compressional waves produced by it in a column of liquid are of short length as compared with the diameter of the plate and of the liquid column. Under these conditions it is found that the velocity of sound, measured by resonance, is independent of the materials or dimensions of the vessel containing the liquid ; the method is thus free from the troublesome corrections that have hitherto been necessary when measuring the velocity of sound in tubes by resonance. Sound-velocities are reported for a number of temperatures for water and for mercury, and for a number of concentrations, each at several temperatures, of solutions of sodium chloride. One concentration of potassium chloride and two of sodium iodide at several temperatures are reported. Several thermodynamic coefficients for water and for mercury have been computed from the results, and good agreement has been found with the work of Bridgman.

A more detailed description of the instrument and its theory will be published in another place.

CXXIII. *On Changes that may take place in the Inter-atomic Internal Energy according to Thermodynamics, and Catalytic Action.* *By* R. D. Kleeman, *B.A., D.Sc.**

§ 1. *The Form of the Equation of State of a Perfect Gas according to Thermodynamics.*

ON allowing a liquid to evaporate the external work w done is given by

$$w=p(v_2-v_1)=\int_{v_1}^{v_2} p\,.\,\partial v, \quad . \quad . \quad . \quad . \quad (1)$$

where p denotes the pressure and v_1 and v_2 the volumes of the liquid and vapour respectively. The internal heat of evaporation L at the absolute temperature T is obtained by multiplying the well-known thermodynamical equation

$$\left(\frac{\partial U}{\partial v}\right)_T+p=T\left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad (2)$$

by ∂v and integrating it between the limits v_1 and v_2, giving

$$U_2-U_1+p\,(v_2-v_1)=L+w=T\int_{v_1}^{v_2}\left(\frac{\partial p}{\partial T}\right)_v.\,\partial v, \quad . \quad (3)$$

where U_2 and U_1 denote the internal energies in the vaporous and liquid states respectively. On differentiating equation (1) with respect to T at constant volume, it may be written

$$\left(\frac{\partial w}{\partial T}\right)_v=\left(\frac{L+w}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

by means of the foregoing equation. Now the writer has shown † that the adiabatic of zero entropy corresponds to $T=0$. Therefore, when $T=0$, we have

$$\frac{L+w}{T}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

* Communicated by the Author.
† Phil. Mag. iv. p. 261 (1927).

and equation (4) under these conditions may be written

$$\left(\frac{\partial w}{\partial T}\right)_v = \frac{\partial}{\partial T}\{p(v_2 - v_1)\} = \left[\frac{\partial}{\partial T}(pv_2)\right]_v = 0, \quad . \quad (6)$$

since v_2 is infinitely large in comparison with v_1 *.

A substance by definition is in the state of a *perfect* gas when its volume is infinitely large. In certain cases, however, a gas may behave as a perfect gas over a region of finite volumes. Let us write the equation of a perfect gas in the form

$$pv = M\xi RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where M denotes the mass of the gas in mols, and ξ a quantity whose nature remains to be determined. On substituting for pv_2 from this equation in the preceding equation, it becomes

$$\left(\frac{\partial w}{\partial T}\right)_v = M\xi R + MRT\left(\frac{\partial \xi}{\partial T}\right)_v = 0 \quad . \quad . \quad (8)$$

It follows from this equation that ξ *is a function of* T *which becomes zero when* $T=0$. We will show presently that it is also a function of the volume v, and that its functional form depends on the nature of the substance.

§ 2. *The Gas Scale and Thermodynamical Scale of Temperature.*

The temperature T in equation (2) refers to the absolute thermodynamical scale of temperature, which is fundamentally defined by the equation

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which refers to a reversible cycle in which Q_1 denotes the heat energy taken in at the temperature T_1, and Q_2 the heat energy given out at the temperature T_2. Hence T in equation (7) also refers to that scale. The scale based on the perfect gas thermometer for which it has been assumed

* Since the result expressed by equation (6) is very important, subsidiary evidence of the truth of equation (5) would be welcome. In a paper that will appear in the May number of the 'Journal of the Franklin Institute,' it is shown that since $T=0$ in equation (5) it follows from the calculus that $L=0$. This result, it is then shown, can also be deduced from Clapeyron's well-known equation referring to the evaporation of a liquid.

that $pv = \mathrm{MRT}$ holds exactly, and the foregoing thermodynamical scale will therefore *not coincide exactly* according to equation (7), but the difference will evidently be negligible except close to the absolute zero.

§ 3. *The Change in Inter-atomic Internal Energy on Change of Volume of a Chemically Non-Interacting Gas.*

On substituting for p in equation (2) from equation (7), it becomes

$$\left(\frac{\partial \mathrm{U}}{\partial v}\right)_{\mathrm{T}} = \frac{\mathrm{MRT}}{v}\left(\frac{\partial \xi}{\partial \mathrm{T}}\right)_{v} \cdot \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thus $\left(\frac{\partial \mathrm{U}}{\partial v}\right)_{\mathrm{T}}$, the change in internal energy per unit change in volume of a perfect gas, is not zero as is usually supposed.

On multiplying the equation by ∂v and integrating it between the limits ∞ and v, supposing that the gas law is obeyed between these limits and that ξ is independent of v, we obtain

$$\mathrm{U}_{\infty} - \mathrm{U}_{v} = \mathrm{MRT}\left(\frac{\partial \xi}{\partial \mathrm{T}}\right)_{v} \{\log \infty - \log v\}, \quad . \quad . \quad (11)$$

where U_{∞} and U_{v} denote the internal energies at the volumes ∞ and v respectively. The right-hand side of the equation is infinite, and hence the gas would undergo, if the supposition made is true that ξ is independent of v, an infinitely large change in internal energy on increasing its volume till it is infinitely large. But this is manifestly absurd, and hence ξ *must be a function of* v *besides of* T, *and of a form which would make the right-hand side of the equation finite.* Its value when v has not very large values will evidently not differ appreciably from unity. But for very large values of v it must differ considerably from unity, otherwise the value of $\mathrm{U}_{\infty} - \mathrm{U}_{v}$ would not be rendered finite.

This result has an important and interesting bearing on the kinetic theory of gases. The pressure according to kinetic theory is given by

$$p = \frac{1}{3}\frac{\mathrm{M}}{v}\mathrm{V}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where V denotes the average velocity of translation of a molecule. From this equation and equation (7) we have

$$\xi \mathrm{RT} = \tfrac{1}{3}\mathrm{V}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

from which it follows that *the kinetic energy of a molecule is not exactly proportional to* T, *and that it also depends on the*

volume of the gas, especially when it is large. The physical significance of this will be discussed in a subsequent paper.

Let us next determine how this change in internal energy on change of volume is produced. Equation (10) may be written

$$\left(\frac{\partial U}{\partial v}\right)_T = CRT\left(\frac{\partial \xi}{\partial T}\right)_v, \quad . \quad . \quad . \quad . \quad (14)$$

where C denotes the concentration in mols. Thus the change in internal energy ∂U depends on the molecular concentration C, or on the average distance of separation of the molecules, and hence it depends on molecular interaction. We may, therefore, also write the equation

$$\left(\frac{\partial U}{\partial v}\right)_T = knT\left(\frac{\partial \xi}{\partial T}\right)_v, \quad . \quad . \quad . \quad . \quad (15)$$

where n denotes the number of times per second each of the molecules in unit volume gets within a distance r of another molecule, and k is a constant. Such an event will be called a chemical collision. Now it will be evident on reflexion that ∂U could only depend on n if a molecule during a chemical collision undergoes a change in internal energy which is not permanent but changes with time. Its average internal energy will then depend on the interval between two collisions, or on n. The distance r, it now appears, is the largest distance two molecules may be separated from each other and still affect each other's internal energy.

The average change in internal energy of a molecule during a collision will evidently depend on its nature, and hence the functional form of ξ of a gas, or the constants it contains, depends on the nature of the molecules. It is, therefore, convenient to write equation (15)

$$\left(\frac{\partial U}{\partial v}\right)_T = n \cdot \psi(n, T, A), \quad . \quad . \quad . \quad . \quad (16)$$

where A is a quantity depending on the nature of a chemical collision, and ψ a function of n, T, and A.

§ 4. *The Change in Internal Energy on Change of Volume of a Chemically Non-Interacting Gaseous Mixture.*

If we consider two isolated non-interacting gases a and e, whose volumes are equal, we have

$$\left(\frac{\partial U_a}{\partial v}\right)_T = n_a \cdot \psi(n_a, T, A_a), \quad . \quad . \quad . \quad (17)$$

$$\left(\frac{\partial U_e}{\partial v}\right)_T = n_e \cdot \psi(n_e, T, A_e), \quad . \quad . \quad . \quad (18)$$

from equation (16), where the suffixes a and e refer to the substances a and e respectively. If the gases are mixed and the volume of the mixture is equal to that of either of the constituents before mixing, it follows from equation (16) that

$$\left(\frac{\partial U}{\partial v}\right)_T = n_a \cdot \psi(n_a, T, A_a') + n_e \cdot \psi(n_e, T, A_e') + n_{ae} \cdot \psi(n_{ae}, T, A_{ae}), \quad . \quad (19)$$

where n_{ae} denotes the number of chemical encounters of the molecules a with the molecules e in unit volume per second, and A_{ae} a quantity depending on the nature of an encounter. The quantities A_a' and A_e' in this equation are not the same as the quantities A_a and A_e in equations (17) and (18), since what now happens when two molecules a chemically encounter each other depends on their previous encounters with molecules e, and hence on previous encounters of molecules e with each other, besides on the previous encounters of the molecules a with each other. Thus $\left(\frac{\partial U}{\partial v}\right)_T$ of a gaseous mixture is not an additive property of the constituents, in other words they affect each other's internal energy. This result, we shall see presently, is very important.

The equation of state of the mixture of gases is

$$pv = (M_a + M_e)\xi_{ae}RT, \quad . \quad . \quad . \quad . \quad (20)$$

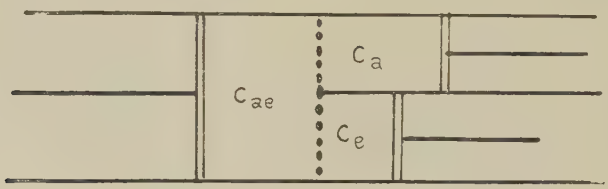
where $(M_a + M_e)\,\xi_{ae}$, according to the foregoing result, is not equal to the sum of $M_a\,\xi_a$ and $M_e\,\xi_e$ referring to the constituents in the isolated state. It may be mentioned here that it will be shown in a separate paper that at the absolute zero of temperature, however,

$$(M_a + M_e)\xi_{ae} = M_a\,\xi_a + M_e\,\xi_e \quad . \quad . \quad . \quad (21)$$

§ 5. *Changes in Internal Energy that Substances undergo on being brought into Contact.*

The effect the constituents of a mixture exert on each other's internal energy may be further studied by means of the apparatus shown diagrammatically in the figure. It consists of a chamber C_{ae} separated from the chambers C_a and C_e by membranes permeable to the substances a and e respectively, the volumes of the chambers being varied by means of pistons. Suppose that the chamber C_{ae} contains a mixture of non-interacting molecules or atoms a and e. The constituents

may be separated from each other by passing them into the chambers C_a and C_e, keeping the pressures in the chambers constant during the process. The constituents will not undergo a change in internal energy during separation since the nature of the mixture in the chamber C_{ae} remains unchanged. Now suppose that the constituents are separated in this way and the volume in each case then increased by v_1. Next suppose that the foregoing process is varied by first increasing the volume of the chamber C_{ae} by v_1, and then separating the constituents similarly as before, in which case the same final volumes are obtained. Now the change in internal energy of the isolated molecules a in the first case on changing the volume from v to v_1 is not equal to the change in internal energy that takes place on changing the volume of the mixture, according to the investigation of the previous Section, or the substance a in the two final states in these processes will not possess the same internal



energies, and the same holds for the final states of the substance e. From this it follows that a substance may permanently change the internal energy of another substance by contact when both are in the perfectly gaseous state. When the substances are not in the perfectly gaseous state the effect is likely to be much more pronounced. Since a change in the internal energy of an atom must be accompanied by a change in its nature, *it follows that the nature of matter is constantly changing*, these changes being, however, as far as we know, immeasurably small, at least in most cases. An atom would accordingly bear the impression of all its previous history.

§ 6. *Contact Catalytic Action.*

If substances undergoing chemical interaction are brought into contact with another substance, a change in the interatomic energies of the interacting substances, we have seen, takes place. The latter substance for convenience may be

in the solid state but exhibiting a large surface, which obtains when the substance is in a finely divided state. This change in internal energy will have the effect of increasing or retarding the rapidity of the interaction, since what happens to two atoms or molecules when they come together evidently depends on their internal energy. *Contact catalytic action, the kind that does not involve a chemical change of the catalysing agent, is thus shown to be physically possible, and a consequence of the Laws of Thermodynamics.* This result should give confidence in the effectiveness of contact catalysing agents and extend their use.

It may be mentioned in this connexion that in a previous paper * the writer has shown that the constant of mass-action K of a gaseous reaction is given by

$$\mathrm{K} = \frac{k_1 \kappa_1}{k_2 \kappa_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where k_1 and k_2 are quantities depending on the chances of molecular collision, and κ_1 and κ_2 quantities depending on the state of the molecules during collision. This state is determined by the previous molecular encounters and therefore depends on the volume of the gas and the masses of the constituents. In the light of the present investigation it appears that *the interacting substances themselves have a catalytic action upon each other*, which is expressed by the quantities κ_1 and κ_2.

In a subsequent paper it will be shown that when the catalytic agent undergoes a chemical change itself a special kind of catalytic effect exists.

§ 7. *The Use of Equation* (7) *in Determining the Functional Nature of the Constant of Mass Action.*

In a previous paper * the writer showed that the constant of mass-action K is in general a function of the volume of the interacting gas and the masses of the constituents besides of the temperature. In a subsequent paper † the writer gave the differential equations by means of which the functional nature of the constant of mass-action may be determined. Using the orthodox gas equation $pv = \mathrm{MRT}$ it was shown that in some cases K is a function of the temperature only. It appears now that strictly equation (7) should be used.

* Phil Mag. v. p. 263 (1928).
† Phil. Mag. v. p. 620 (1928).

Since ξ in the equation is a function of v (but whose exact form is not yet known), it appears that in the foregoing cases K will now be obtained as a function of the volume and the masses of the constituents, but appreciable only when the volume is very large. In exceptional cases only it appears, which may even not exist, may K be *strictly* a function of the temperature only.

CXXIV. *The Crystal Structure of α-Manganese.* *By* G. D. Preston, *B.A., The National Physical Laboratory* *.

[Plates XVIII. & XIX.]

Introduction.

THE crystal structure of the allotropes of manganese has been the subject of three investigations. The α-modification, stable at room temperatures, has been examined by the powder method by Bradley † and by Westgren and Phragmén ‡. The latter investigators found that the lines of a powder X-ray photograph could be accounted for by a cubic structure of side $a = 8{\cdot}894 \pm 0{\cdot}005$ Å., the unit containing 56 atoms giving a density 7·21 g./cm.^{3} as compared with a figure 7·39 g./cm.^{3} given by Kaye and Laby.

In a subsequent paper Bradley and Thewlis § have shown that the number of atoms associated with the unit is 58, and, using the intensity of the reflexion as observed by Westgren and Phragmén, they have given values for the parameters which fix the positions of the atoms within the unit.

The present paper contains an account of experiments which have been done using single crystals of manganese. In a structure of such complexity it appeared very desirable to supplement the results of the powder method by the Laue and oscillating crystal methods. The results of the experiments to be described are in agreement with the structure proposed by Bradley and Thewlis, and are now offered as an experimental verification of the deductions from the powder method.

* Communicated by Dr. W. Rosenhain, F.R.S.
† Bradley, Phil. Mag. vol. l. p. 1018 (1925).
‡ Westgren and Phragmén, *Zeit. f. Phys.* vol. xxxiii. p. 777 (1925).
§ Bradley and Thewlis, Proc. Roy. Soc. A, vol. cxv. (1927).

Material.

The material used for the X-ray investigation has been made available by the development of a method of purifying manganese by distillation *. The sublimate consists of small lumps of manganese † which can be broken up and the fragments examined by the Laue method to ascertain if they are single crystals. After several trials a suitable specimen was obtained.

Laue Photograph.

The Laue photograph obtained from the specimen finally selected is shown in fig. 1 (Pl. XVIII.). The crystal has been oriented so that the incident beam of X-rays is parallel to an axis of tetragonal symmetry. Rotation through 90° about the proper axis produced a similar photograph, and a photograph showing trigonal symmetry was obtained when the crystal was set at the calculated angles. These photographs show that the material has cubic symmetry. The photographs also show that the specimen consists of more than one crystal, the reflexions from which interfere with the symmetry of the picture to some extent. In spite of this complication all the photographs obtained from different specimens during the search for the one finally selected have shown symmetry of the type O_h, which places the crystal in one of the groups T_d, O, or O_h.

Oscillating Crystal Method.

The presence of more than one crystal complicated the application of this method. To eliminate the reflexions from the crystals not under examination the following scheme was used. Eight photographs in all were taken, the axis of oscillation being (001). In the first photograph the (100) direction oscillated through a range from 0° to 12° from the incident beam of X-rays. In the fifth photograph the range of oscillation of (100) was 0° to −12° from the X-ray beam. Owing to the symmetry of the crystal the right-hand side of the first photograph should be identical with the left-hand side of the fifth as far as reflexions from the crystal under examination are concerned. The other crystal or crystals with a random orientation will give reflexions which, if they appear in the left-hand side in the first photograph, will not appear on the right-hand side of the fifth. Denoting the left hand-side of the first photograph by 1 L and the

* M. L. V. Gayler, Journ. Iron and Steel Inst. vol. cxv. p. 393 (1927).
† *Ibid.* p. 408, pl. xxxv. fig. 4.

right-hand side by 1 R, the following scheme shows the ranges of oscillation and the correspondence between the photographs :—

Range of Oscillation.	Photo.			Photo.	Range of Oscillation.
0° to 12°	1 L	identical with		5 R	0° to −12°
	1 R	,,	,,	5 L	
10° to 22°	2 L	,,	,,	6 R	−10° to −22°
	2 R	,,	,,	6 L	
20° to 32°	3 L	,,	,,	7 R	−20° to −32°
	3 R	,,	,,	7 L	
30° to 42°	4 L	,,	,,	8 R	−30° to −42°
	4 R	,,	,,	8 L	

As an example of the sort of photograph obtained Nos. 4 and 8 are reproduced in fig. 2 (Pl. XIX.). Assuming that the unit cube has a side of 8·89 Å., as found by Westgren, the planes (hkl) which should appear on the different photographs were determined by the method described by Bernal *. No reflexions were observed on the photographs which could not be accounted for by a cube of this size. Had a wrong choice been made reflexions would have appeared when not expected, so that the results confirm the fact that the unit has a side approximately 8·89 Å. No reflexions were observed other than those for which $h+k+l$ is even, indicating that the lattice is body-centred. Westgren and Phragmén, in the work already referred to, recorded a weak reflexion corresponding to the plane (320), but no trace of this could be found on the photographs 1 L, 5 R, 2 L, 6 R, 3 R, or 7 L where it should have appeared. With this exception the values of $(h^2+k^2+l^2)$ recorded by Westgren and Phragmén are all even, in agreement with the results of the present investigation.

The results of a careful comparison of the pairs of photographs are given in Table I., from which, for the sake of brevity, values of (hkl) which make $h+k+l$ odd have been omitted. In the first column are given the values of $h^2+k^2+l^2$, in the second the corresponding values of (hkl). In the third the appropriate value of $\sin\theta$, the angle of reflexion, calculated for the K_α radiation of iron ($\lambda=1{\cdot}932$ A.) and a cube of side 8·89 Å. The K_β radiation of iron is strongly absorbed by manganese, and reflexions arising from it are not observed on any of the films. The next eight columns of the table correspond with the eight photographs. Each of these eight columns is subdivided into three, the first of which contains a figure 0, 1, 2, 3, or 4, giving the value of the index

* Bernal, Proc. Roy. Soc. A, vol. cxiii. p. 117 (1926).

Σh^2.	*hkl*.	sin θ.	*l*.	1L.	5R.	*l*.	1R.	5L.	*l*.	2L.	6R.	*l*.	2L
2	110	·154	...	...	...	1	...	...	...	...	...	1	..
4	200	·217	...	...	...	0	...	...	...	...	...	0	..
6	211	·266	1/2?	...	...	...	...	..	1/2	...	...	...	..
8	220	·307	...	...	...	...	...	...	...	...	..	2?	..
10	310	·343	...	...	...	0?	...	...	...	...	...	1	..
12	222	·376	...	...	...	...	...	...	2	3	3	...	..
14	321	·406	1	...	...	2	...	...	1/3	...	...	2/3	..
16	400	·435	...	...	...	...	...	...	...	...	...	...	..
18	330	·461	...	...	...	...	..	...	0	>10	>10	...	..
	411		...	...	...	..	...	...	...	...	...	1	1(
20	420	·486	...	...	...	0	...	...	...	...	...	...	..
22	332	·510	2	10	10	3	10	10	2/3	>10/>10	>10/>10	3?	8
24	422	·532	...	...	...	2	8	9	...	...	...	2?	6
26	431	·554	1/4	9	9	1?	4	...	1	8	8	...	..
	510		...	...	...	...	...	...	...	...	...	0?	..
30	521	·595	...	...	...	...	...	...	...	...	...	1	1
32	440	·610	0	1	1	...	...	...	...	...	...	...	..
34	433	·634	3	2	2	3	1	1	...	...	...	3/4	3
	530		...	...	...	0	...	...	0	...	...	0?	..
36	442	·652	2/4	5	5	2?	...	5	...	...	...	...	..
	600		...	...	...	...	...	...	...	...	...	...	..
38	532	·670	2?	1?	...	...	...	...	2/3	1/2	1/2	2	3
	611		...	...	...	...	...	...	...	...	...	...	..
40	620	·687	...	...	..	...	...	...	...	...	...	...	..
42	541	·704	1	...	...	1	...	...	4	...	...	...	..
44	622	·720	...	...	...	...	...	...	2?	2	...	...	..
46	631	·735	...	...	...	...	...	..	1	2	2	1?	1
48	444	·752	...	...	...	...	...	...	...	...	...	4	8
50	543		...	...	...	3/4	...	1	...	...	...	3/4	1
	550	·768	...	...	...	0	10	10	...	...	...	...	..
	710		...	...	...	...	...	...	...	...	...	...	..
52	640	·783	0	...	..	...	...	...	4	...	...	0	..
54	552		...	...	...	2	8	8	...	...	...	2	9
	633	·798	3	9	10	...	...	...	..	...	...	...	..
	721		...	...	...	...	...	..	1	9	9	...	..
56	642	·813	2?	...	2	2/4	8/7	8/7	...	...	...	...	..
58	730	·827	0	7	8	...	...	...	0	6	6	...	..
62	651	·856	...	...	...	1	5	6	...	...	...	1*	7
	732		2/3	5/6	6/5	...	...	...	...	...	...	...	..
64	800	·869	..	...	...	...	...	...	..	...	...	...	..
66	554 off plate.												
	741	·882	...	...	...	1	4	4	...	...	...	...	..
	811		...	...	...	...	...	...	1	4	4	...	..
68	644 off plate.												
	820	·896	0	4	2	...	...	...	0/2	6/6	6/1	...	..
70	653	·909	...	...	...	...	...	...	...	...	...	...	..
72	660	·922	...	...	...	...	...	...	...	...	...	0	10
	822		2	10	10	...	...	...	...	...	...	...	..
74	743		...	...	...	...	...	...	...	...	...	3	..
	750	·934	...	...	...	0?	...	...	...	...	...	0	..
	831		1/3	...	1	1/3	5/6	5/6	3	5	5	...	..
76	662	·947	...	...	...	...	...	...	...	...	...	...	..
78	752	·960	...	...	...	...	...	...	...	...	...	2?	..
80	840	·972	...	...	...	0	...	...	...	...	...	0	2
82	910	·984	0	...	...	...	...	...	0/1	...	...	...	..

* 651 and 561 both appear on this

[*To face page* 1200.

	3L.	7R.	*l.*	3R.	7L.	*l.*	4L.	8R.	*l.*	4R.	8L.	I.	
?	...	...	...	..	...	0	...	...	...	.	..	..	0
	...	...	...		...	...	...	...	...	..	...	...	0
	...	...	...	...	...	...	...	...	1?	...	...	...	0
	...	...	2?	...	...	...	...	..	...	...	...	...	0
	...	..	1	...	...	...	...	...	0	...	?	...	0
	...	3	...	...	...	...	...	...	...	...	..	3	25
	...	...	...	...	...	1/2	...	...	...	...	...	...	0
	...	...	0	6	7	...	...	...	...	...	...	$6\frac{1}{2}$	60
	...	...	...	...	...	...	...	...	3	10	10	10	200
	...	...	...	...	..	...	...	...	1	9	10	10	200
	...	...	2	...	...	0	...	...	2	...	...	...	0
	...	...	...	...	...	...	..	...	...	...	...	10	200
	6	9	4	...	...	...	...	...	...	...	...	8	100
	6	...	3	7	7	3	6	7	3?	4	5	8	100
	...	.	0	...	...	...	...	...	1	5	6	6?	50?
	...	...	2	1	2	1/2	1/1	2/1	...	...	...	1	15
	...	...	..	...	...	4	...	...	...	...	...	1	15
	...	...	...	...	...	...	...	...	...	...	...	2	20
	...	...	...	...	...	3	...	...	...	...	...	...	0
	...	...	...	...	...	...	...	...	4	...	...	5	40
	...	...	...	...	...	...	...	.	0	...	...	...	0
	...	...	3	3	2	...	...	...	...	...	...	2	20
	...	...	1?	...	...	1	...	...	1	...	...	...	0
	...	...	0	...	...	...	...	...	...	...	...	...	0
	...	...	...	...	...	4	...	...	...	...	...	...	0
	3	4	2	5	5	...	...	...	2	5	6	5	40
	1	1	1?	...	3	...	...	...	...	...	...	2	20
	...	...	4?	...	...	...	..	...	...	...	...	8	100
	...	...	3?	...	...	...	...	...	4	...	...	1	15
	...	...	...	...	...	...	...	...	...	...	...	10	200
	...	...	...	...	...	0/1	...	...	0	...	..	...	0
	...	...	...	...	...	...	...	...	...	...	...	...	0
	...	...	...	...	...	...	...	...	...	...	...	9	140
	...	...	...	...	...	...	...	...	3	8	9	9	140
2	5/8	9/8	...	...	...	2	9	9	1	9	10	9	140
	...	...	2	8	8	4	5	6	...	...	...	8	100
	7	7	0?	5	...	...	...	..	0	5	8	7	70
	...	...	1	4	5	...	...	...	...	...	...	5	40
	...	...	...	...	...	3	3	4	2	5	5	5	40
	...	...	...	...	...	0	...	...	...	...	...	...	0
	...	...	1?	...	...	...	...	...	1	2	4	4?	30?
	...	5	...	...	...	1	4	4	...	...	...	4	30
	5	6	...	...	...	0	6	7	...	...	...	6	50
	...	...	3	5	6	...	...	...	3	6	7	6	50
	...	...	0	9	10	...	...	...	...	...	...	10	200
	9	5	...	...	...	2	10	10	...	...	...	10	200
	...	...	3	...	...	3	4	4?	...	...	...	4?	30?
	...	...	0	...	...	...	...	...	0	...	...	...	0
	...	...	...	...	..	1	5	5	...	...	...	5	40
	...	...	2	6	6	...	...	..	2	7	8	7	70
	...	...	2	8	8	...	...	...	...	.	...	8?	100?
	...	...	...	...	...	0	1	3	...	...	...	2	20
	...	...	...	...	...	...	...	...	...	...	...	...	0

the great intensity.

l which determines the "layer" line on which the reflected spot is calculated to fall. An entry in this column means that a reflexion is to be expected on the corresponding photograph. The next two columns contain figures which give the intensity of the observed spots on each of a pair of corresponding photographs. A rough estimation of the intensity is all that has been attempted. For this purpose a photographic plate was exposed under a sheet of lead in which ten small holes had been drilled. These holes were covered with 0, 1, 2 . . . 9 sheets of copper 0·05 mm. thick. The diffraction spots on the X-ray photograph were then compared with this arbitrary intensity scale, and the figures are those entered in the columns under 1 R, 5 L, etc., in Table III. The following Table shows approximately the relation between the intensity and the number given in Table I. :—

No.....	10	9	8	7	6	5	4	3	2	1
Intensity.....	200	140	100	70	50	40	30	25	20	15

The means of the observed intensities have been entered in the last column of Table I. In the majority of cases the agreement between different photographs is tolerably good, but where doubt arises the larger figures have been chosen, because it appeared more probable that a reflexion should be too weak than too strong. This arises from two causes:— the crystal may come into the reflecting position near the end of its nominal range of oscillation and a small error in setting might prevent the reflecting position ever being attained ; for instance, this has been the cause of the small intensity of (332) in photograph 6 L and of the absence of (431) in 5 L. The possibility of a plane being absent from this cause has been indicated by a question mark after the figure giving the value of l in the table. Again, the intensity may be weakened by the obstruction to the passage of X-rays offered by the small crystals associated with the one under examination.

For the most part, however, there is not much doubt about the order of intensity. Of the 53 planes recorded in the table doubt exists as to the intensity of four, namely (510), (741), (743), and (752).

Before proceeding to make use of the intensity of reflexions to place the atoms within the unit it is necessary to fix the number of atoms within the cell. For this purpose the density (ρ) and side (a) of the unit must be determined. These quantities are connected by the relation

$$\frac{n\mathrm{M}}{a^3} = \rho,$$

where M is the weight of the manganese atom in grammes and n is the number of atoms associated with the cell.

Density and Parameter of Unit.

The density was determined by weighing the powder in a specific-gravity bottle, the liquid used being CCl_4, as the powder oxidizes rapidly in contact with water. About 50 g. of distilled manganese were ground in an agate mortar and passed through a sieve of 200 meshes to the inch. The determination of density was made in the usual way: the weighed powder in the specific-gravity bottle of about 11 c.c. capacity having been covered with CCl_4 was placed in a receiver, which was then exhausted until the liquid boiled. The bottle was then filled with the liquid in a thermostat at 25·0° C. As the cap on the bottle did not fit sufficiently tightly to prevent evaporation, weighings were taken at 5 min. intervals and the true weight was determined by extrapolation. The loss of weight due to evaporation was quite small, amounting to about 0·1 mg. per minute. Owing to the small amount of material available it was not possible to make the determination to more than three figures. The results of two determinations were 7·445 and 7·437 g./cm.^{3}, whence it may be inferred that the density is not less than 7·44 g./cm.^{3} since the errors are likely to lead to too small a value.

The parameter of the lattice was determined from an X-ray photograph of powdered material. The camera was of the Seeman focussing type, and its constants had been previously determined by a calibration photograph of powdered rock-salt. The mean value of the parameter was found to be $8{\cdot}894 \pm 0{\cdot}002$ Å., as shown in Table II., in agreement with the value given by Westgren and Phragmén in the paper already referred to.

Table II.

$\log \sin \theta$.	$h^2+k^2+l^2$.	λ.	a.
9657	72	α_2	8·892 Å.
9645	...	α_1	8·896
9521	68	α_1	8·896
9456	66	α_1	8·896
9330	62	α_2	8·896
9321	...	α_1	8·894
9177	58	α_1	8·893
9099	56	α_1	8·897
9022	54	α_1	8·893
8855	50	α_1	8·892

Mean $a = 8{\cdot}294 \pm {\cdot}002$

Taking the atomic weight of manganese to be 54·93 (O = 16) and the weight of the hydrogen atom to be $1{\cdot}663 \times 10^{-24}$ g. with the atomic weight of hydrogen equal to 1·008 (O = 16), the above values of the density and parameter give

$$n = \frac{\rho a^3}{\mathrm{M}} \leqslant 57{\cdot}7,$$

or within the limits of accuracy to which ρ is known, $n = 58$.

To complete the solution of the structure we have now to assign positions to the 58 atoms within the unit so as to account for the observed intensities of the reflexions of the oscillating crystal photographs. The Laue photograph shows symmetry of the type O_h, so that the crystal has the symmetry of one of the point groups T_d, O or O_h. The oscillating crystal photographs show reflexions from planes (hkl) only when $h+k+l$ is even. The lattice is, therefore, body-centred. Of the space-groups isomorphous with these point-groups only six, viz., T_d^3, T_d^6, O_5, O_8, O_h^9 and O_h^{10} are constructed on a body-centred lattice.

Reference to Wyckoff ('The Analytical Expression of the Results of the Theory of Space Groups') shows that the groups T_d^6, O_8, and O_h^{10} may be eliminated. In the case of T_d^6, for instance, the equivalent positions contain 12, 16, 24, or 48 points, so that the number, n, of atoms within the unit must be expressed by

$$n = 12p + 16q + 24r + 48s,$$

where p, q, r, and s are integers or zero. It follows that n must be a multiple of 4, and in the case under consideration we know that $n = 58$, which is not a multiple of 4. An exactly similar argument excludes the possibility of α-manganese belonging to either of the groups O_8 or O_h^{10}.

According to the tables of Astbury and Yardley *, the group T_d^6, in addition to the halving of the spacing when $h+k+l$ is odd, is characterized by the spacing hhl being quartered if l is odd, normal if $l = 2x$ (x odd) and halved if $l = 2x$ (x even or zero). The last condition is not fulfilled by the X-ray spectra of α-manganese, because 330 and 550 and 114 are all very intense. The same objection arises in the case of O_h^{10}, so that on these grounds also these groups must be rejected. We have, therefore, to place the atoms in the unit in positions in accord with the symmetry requirements of one of the groups T_d^5, O_5, or O_h^9.

* Phil. Trans. Roy. Soc. A, vol. ccxxiv. p. 255.

Bradley and Thewlis place the crystal in the group T_d^3, the 58 atoms being divided into four sets, two of 24, one of 8, and one of 2 atoms. The coordinates within the unit are as follows :—

24 Equivalent positions :

$u\ u\ v$ $\bar{u}\ u\ \bar{v}$ $u+\frac{1}{2}$ $u+\frac{1}{2}$ $v+\frac{1}{2}$, etc.
$v\ u\ u$ $\bar{v}\ \bar{u}\ u$
$u\ v\ u$ $u\ \bar{v}\ u$
$u\ \bar{u}\ \bar{v}$ $\bar{u}\ \bar{u}\ v$
$\bar{v}\ u\ \bar{u}$ $v\ \bar{u}\ \bar{u}$
$\bar{u}\ \bar{v}\ u$ $\bar{u}\ v\ \bar{u}$

8 Equivalent positions :

$u\ u\ u$ $u+\frac{1}{2}$ $u+\frac{1}{2}$ $u+\frac{1}{2}$, etc.
$\bar{u}\ u\ \bar{u}$
$u\ \bar{u}\ \bar{u}$
$\bar{u}\ \bar{u}\ u$

2 Equivalent positions :

$0\ 0\ 0$ $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$.

The values of the coordinates given by Bradley and Thewlis expressed in degrees are

24 (1) $u_1 = 128$ $v_1 = 15$
24 (2) $u_2 = 32$ $v_2 = 100$
8 $u = 114$.

Prior to the publication of the paper by Bradley and Thewlis an almost identical result had been obtained from the intensities of the photographs given in Table I. The values found for the coordinates were

24 (1) $u_1 = 125^\circ$ $v_1 = 20^\circ$
24 (2) $u_2 = 33^\circ$ $v_2 = 101^\circ$
8 $u = 115^\circ$

in very close agreement with the results of Bradley and Thewlis. The values of the coordinates given by Bradley and Thewlis afford a somewhat better account of the intensities, so the "structure factor" has been computed for these values for the planes recorded in Table I. The intensity of reflexion I is given by

$$I = k(A^2 + B^2),$$

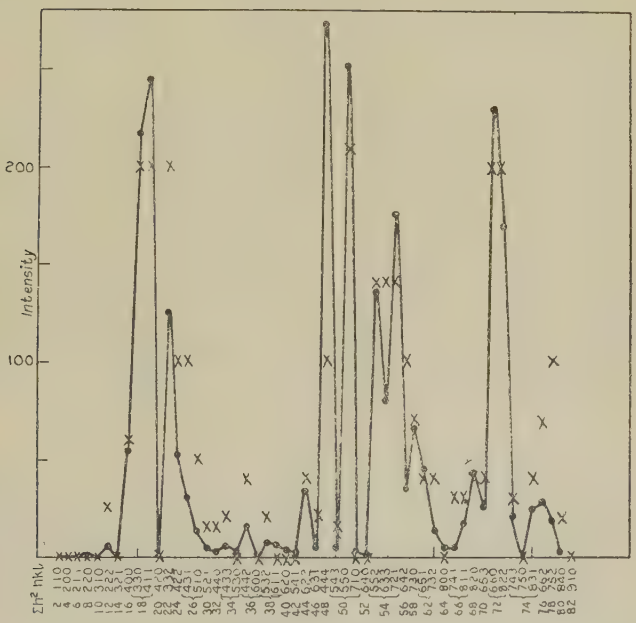
where k is some function of the angle of reflexion, and

$$A = \Sigma \cos 2\pi(hx_s + ky_s + lz_s),$$
$$B = \Sigma \sin 2\pi(hx_s + ky_s + lz_s),$$

(x_s, y_s, z_s) being the coordinates of the sth atom within the unit. The contribution to A from 24 atoms whose coordinates are fixed by the parameters (uuv) reduces to

$$8\,(\cos 2\pi uh \cos 2\pi uk \cos 2\pi vl + \cos 2\pi uh \cos 2\pi vk \cos 2\pi ul + \cos 2\pi vh \cos 2\pi uk \cos 2\pi ul),$$

Fig. 3.



while the contribution from 8 atoms whose position is fixed by the parameter u is

$$8 \cos 2\pi uh \cos 2\pi uk \cos 2\pi ul,$$

with similar expressions involving sines for the contributions to the factor B.

The quantities A and B having been computed from the above expressions, $A^2 + B^2$ is plotted on an arbitrary scale as shown in fig. 3, the calculated points being joined by a continuous line. The intensities as observed are marked in

the same figure with a cross. It will be seen that there is a very general agreement as to the order of intensity; where the calculated intensity is great the observed intensity is also great, the agreement extending over a wide range of values of (*hkl*). In view of the very rough nature of the estimation of the intensity, the agreement is quite as good as can be expected. No attempt has been made to integrate the intensity, so that a reflexion such as 444 appearing in the fourth layer line and covering a comparatively large area on the film would appear too weak. The values of A^2 and B^2 vary so rapidly, especially for large values of h, k, and l, that it is possible to choose values of the parameters within one or two degrees which give the best representation of the observed intensities, even when these are only approximately known.

As regards the possibility of the crystal belonging to either of the groups O^5 or O_h^9, it has not been found possible to account for the observed intensities by any set of equivalent points characteristic of these groups. The values of the variable parameters fixing the positions of the atoms for any group of equivalent points is limited by the consideration that the centres of atoms cannot approach one another too closely. It has been assumed that the "diameter" of the manganese atom is not less than 2A°, and subject to this assumption T_d^3 is the only group that has been found to afford an explanation of the observed intensities.

Summary.

Laue photographs of α-manganese show that this material crystallizes in the cubic system. The oscillating crystal method shows that the lattice is of the body-centred type, and a powder photograph gives the side of the cube as 8·894 $\pm$0·002 Å. The density is determined to be 7·44 g./cm.^{3}, requiring 58 atoms to be associated with the unit. The observed intensities of reflexion of the oscillating crystal photographs are satisfactorily accounted for by placing the crystal in the space group T_d^3.

The author desires to express his thanks to Dr. Marie L. V. Gayler for supplying the material which made the work possible, and to Dr. Rosenhain for his continued interest in and encouragement of the research.

CXXV. *The Crystal Structure of β-Manganese.* *By* G. D. Preston, *B.A., The National Physical Laboratory* *.

[Plate XX.]

Introductory.

X-RAY examinations of the structure of the allotropic modifications of Manganese have been carried out by Bradley † and by Westgren and Phragmén ‡. Bradley demonstrated the existence of two different forms of Manganese, and Westgren and Phragmén, whose work was published at the same time as Bradley's, showed that the lines of the powder photograph of β-manganese could be accounted for by a cubic structure of side 6·289 ± 0·004 Å. The presence of three weak lines on their photographs led them to suppose that, if these lines were due to the manganese and not to some impurity, the parameter might be double the above figure, the number of atoms associated with the unit being 20 or 160, according as the smaller or larger figure is the correct one.

In the present investigation an attempt has been made to supplement the information derived from the powder method by that obtained from the Laue and the oscillating crystal methods. The results have made it possible to assign the crystal to its space group and to place the atoms within the unit.

Material.

The material used for the Laue and oscillating crystal methods was similar to that used in the investigation of the structure of α-manganese §. Some of the distilled material, consisting of the α-modification, was annealed at a temperature of 975° C. and quenched in water. This treatment preserves the β-modification by suppressing the change which on slow cooling would take place at 742° C.‖ The material so obtained is somewhat ductile, and attempts to obtain single crystals by breaking small lumps in an agate mortar were useless, as the crystals became deformed in the process. It was found that deformation of the crystals could

* Communicated by Dr. Walter Rosenhain, F.R.S.

† Bradley, Phil. Mag. l. p. 1018 (1925).

‡ Westgren & Phragmen, *Z. für Phys.* xxxiii. p. 777 (1925).

§ *Suprà*, p. 1198.

‖ M. L. V. Gayler, J. Iron and Steel Inst. cxv. p. 393 (1927).

be avoided by etching small pieces of the quenched metal in dilute hydrochloric acid. After a few minutes' treatment in the acid the lumps could be crumbled between the fingers, and specimens so obtained yielded satisfactory Laue photographs, showing no serious signs of deformation. It was not possible by this means to obtain a specimen consisting of one crystal only, so that the information yielded by the oscillating crystal photographs was not so complete as would otherwise have been the case. In spite of this they yielded valuable information, to be described below. The search for a suitable specimen to be subjected to X-ray analysis is exceedingly laborious, much time having been expended in isolating the specimen, the results obtained from which will now be described.

The Laue Method.

A small specimen exposed for two hours in a beam of X-rays from a Coolidge tube with a tungsten target operated at 70 k.v. and 3 m.a., yielded the photograph shown in fig. 1 (Pl. XX.) after the necessary adjustment in orientation had been made. A similar photograph was obtained when the specimen was rotated through 90° about the proper axis. Both photographs show that the X-ray beam is parallel to an axis of tetragonal symmetry, proving that the crystal is cubic and belongs to one of the space-groups isomorphous with the points groups T_d, O, or O_h. It is evident from the photograph that the specimen consists of more than one crystal.

The Oscillating Crystal Method.

The same specimen was used in an attempt to apply the oscillating crystal method to determine the structure of the crystal. The method described in the account of the structure of α-manganese was applied to eliminate the effects of the crystals associated with the one under examination, but, unfortunately, the extra crystals were in this case too numerous to allow the method to be employed with complete success. As in the case of α-manganese, radiation from an iron target was used, the range of oscillation in each photograph being 12° and the exposure 3½ hours, with a current of 8 to 10 m.a. passing through the tube. The presence of the crystals not under examination led to the appearance of a large number of reflexions on all the photographs. The values of $\sin\theta$ for all these reflexions, however, correspond to those to be expected from a cubic structure of side

6·29 Å. No reflexions have been found on any of the photographs which would necessitate the choice of a larger unit, particular attention having been paid to the possibility of the occurrence of the three reflexions recorded by Westgren and Phragmén, which do not agree with the results to be expected from the smaller unit. No trace of these could be found on any of the photographs. It may here be pointed out that of these lines the one for which $\sin^2\theta = 0{\cdot}214$ * corresponds exactly with a line observed by the same authors in the spectrum of α-manganese to which the corresponding value of Σh^2 is 13. This last line has been found by Bradley and Thewlis† to be spurious, and was not observed in the oscillating crystal photographs of α-manganese. There is, therefore, reason to doubt the existence of one of these lines, and careful search has failed to reveal any trace of either of the others on the oscillating crystal photographs of β-manganese. The presence on these photographs of reflexions due to crystals other than the one under examination adds to the possibility of finding any of these reflexions if they existed. There is no reason for ascribing to the unit a side greater than 6·29 Å. so far as can be ascertained by an inspection of the oscillating crystal photographs. A complete analysis of each photograph, on the lines adopted in the case of α-manganese, has been attempted, but many of the reflexions to be expected are absent, because the reflected beam has been absorbed in the stray crystals. In spite of this, much useful information has been obtained from the photographs and is recorded in Table I., column 4. The information of greatest use is that obtained in cases of such planes as (300) and (221), for which $h^2+k^2+l^2$ is the same. On the powder photograph the lines due to reflexions from these planes are superposed, and it is impossible to tell how the intensity is distributed between the two planes. With the oscillating crystal method this is not the case, and in the present instance it is found that (221) is very strong and no reflexion is observed from (300). This fact, by itself, would hardly be sufficient evidence on which to base the conclusion that reflexion from (300) is absent, but when the photograph on which it should appear is examined, it is found that the reflexions to be expected from (410), (520), and (301), to mention no more, are observed. There is, therefore, some evidence to show that the absence of reflexion from the (300) plane is not due to the obstruction of the reflected ray by other

* See Table 3, p. 78, *loc. cit.*

† Proc. Roy. Soc. A, cxv. p. 458 (1927).

TABLE I.

Σh^2.	*hkl*.	sin θ.	Oscillating Crystal.		Powder.				
					Order of Intensity.				
			I.	A^2+B^2.	$\frac{N(A^2+B^2)}{\Sigma h^2}$.	W. & P.	Calc. I.	Observed.	Calc. II.
1	100	0·1535	—	0	0	—	—	—	—
2	110	0·217	w	0·4	2·4	—	26	—	21
3	111	0·266	—	1·0	2·7	vw	25	—	22
4	200	0·307	—	0	0	—	—	—	—
5	210	0·343	mw	1·9	9·1	m	18	—	17
6	211	0·376	—	0·4	1·6	—	30	—	28
8	220	0·435	w	1·6	2·4	—	26	—	27
9	300	0·461	—	0	272·0	s	1	1	1
	221		vs	102 0					
10	310	0·486	vs	67·8	163·0	s	2	4	2
11	311	0·509	s	41·1	89·6	s	5	6	5
12	222	0·532	—	0·5	0·3	—	32	—	32
13	320	0·554	w	1·1	2·0	w	28	—	29
14	321	0·575	ms	8·4	28·8	s	12	9	13
16	400	0 614	—	0	0	—	—	—	—
17	410	0·633	w	2·8	4·0	w	22	—	25
	322		—	0·0					
18	330	0·652	—	0·3	30·5	m	11	9	12
	411		s	22·7					

19	331	0·670	—	0·3	0·4	—	31	—	31
20	420	0·687	ms	23·8	28·6	m	13	—	14
21	421	0·704	—	0·8	1·8	—	29	—	30
22	332	0·721	w	4·7	5·1	w	21	—	23
24	422	0·752	ms	9·1	9·1	—	18	—	20
25	430	0·768	m	10·1	9·7	w	16	—	19
	500		—	0					
26	431	0·783	vs	67·6	142·2	vs	3	3	3
	510		ms	18·6					
27	333	0·798	—	1·6	25·3	m	14	11	15
	511		s	27·9					
29	432	0·827	vs	46·1	127·2	vs	4	2	4
	520		vs	61·5					
30	521	0·841	ms	24·3	38·9	m	7	11	11
32	440	0·869	—	7·4	2·8	—	24	—	26
33	522	0·882	—	0·5	3·6	—	23	—	24
	441		—	4·5					
34	(433)*	0·896	—*	10·4	9·3	—	17	—	18
	530		mw	2·7					
35	531	0·908	vs	26·4	36·2	—	8	8	10
36	442	0·922	vvs	77·1	51·4	—	6	5	6
	600		—	0					
37	610	0·934	vs	51·9	33·6	—	9	13	9
38	(532)	0·946	—*	18·9	32·3	—	10	13	8
	611		ms	13·3					
40	620	0·972	ms	12·2	7·3	—	20	—	16
41	(443)*	0·984	—*	5·8	19·1	—	15	7	7
	540		—	1·9					
	621		ms	12·5					

* Outside limits of film in oscillating crystal photographs.

crystals. The remaining planes of the structure have been dealt with in the same way and the result entered in the table, the intensities being denoted by very strong (vs), strong (s), medium strong (ms), medium (m), and weak (w).

With the exception of the three planes mentioned above, the results of the present investigation are in good agreement with those of Westgren and Phragmén, as is seen by comparison of columns 4 and 7 of Table I. The latter column contains the intensities of the lines observed by Westgren and Phragmén up to the plane (521), the limit imposed by the use of radiation from a chromium target. Some further information as to the intensities of planes up to $h^2+k^2+l^2=41$ is given by the use of iron radiation. In fixing the position of the atoms within the unit it is planes with large values of h, k, and l which are the most sensitive in determining the values of the parameters.

Number of Atoms in the Unit.

There are no available data as to the density of β-manganese, but it seems certain that on cooling the material undergoes a marked contraction on changing into the α-modification. The density must, if this is the case, be less than 7·45 g./cm.^{3}, which is known to be the figure for α-manganese. If there are n atoms of mass M within a cubic unit of side a, then the density ρ is given by

$$\rho = \frac{n\mathrm{M}}{a^3}.$$

In the present case

$$\mathrm{M} = 54{\cdot}93 \times 1{\cdot}65 \times 10^{-24}\ \text{g.} \quad \text{and} \quad a = 6{\cdot}29 \times 10^{-8}\ \text{cm.},$$

so that

$$\rho = 0{\cdot}3645\, n\ \text{g./cm.}^3$$

The most probable value for n is 20, giving a density of 7·29 g./cm.^{3}. These atoms have to be arranged within the unit so as to satisfy the symmetry requirements of one of the cubic space-groups and so as to afford an account of the observed intensities of reflexion.

Determination of the Space-Group.

The results of the oscillating crystal method and of the powder method show that the lattice is of the simple cubic type, for the fact that the planes (310) and (311) give first

order reflexions excludes the possibility of the lattice being either face-centred or body-centred. Reference to the tables of Astbury and Yardley * show that the only possible groups which will yield a Laue photograph of full O_h symmetry and have a simple cubic lattice are T_d^1, T_d^4, O^1, O^2, O^6, O^7, O_h^1, O_h^2, O_h^3, and O_h^4. The same tables show that the groups T_d^4, O_h^2, and O_h^3 are impossible because they are characterized by the absence of odd order reflexions from planes ($hh\,l$) when l is odd, but the plane 113 is observed. O_h^4 is excluded because the spacing (hko) should be halved if $h+k$ is odd, but (320) and (500) or (430) are observed, as reference to Table I. will show. The choice of space-group is, therefore, reduced to one of T_d^1, O^1, O^2, O^6, O^7, or O_h^1. It was not found possible to account for the intensities of reflexion by any permissible choice of coordinates for the group T_d^1. On the other hand, the group O^7 (or O^6, which differs from it only in having an opposite sense of rotation of its screw axes) provides a satisfactory account of the observed reflexions. Reference to Wyckoff † shows that a possible arrangement of 20 atoms in this group is in two sets, one of 12 and the other of 8, whose positions in the unit are as follows :—

12 atoms.

$$\tfrac{3}{4}-u,\ u,\ \tfrac{3}{8}\ :\ \tfrac{1}{4}-u,\ \tfrac{1}{2}-u,\ \tfrac{5}{8}\ :\ u+\tfrac{1}{4},\ u+\tfrac{1}{2},\ \tfrac{1}{8}\ :\ u+\tfrac{3}{4},\ \bar{u},\ \tfrac{7}{8}\ :$$
$$\tfrac{3}{8},\ \tfrac{3}{4}-u,\ u\ :\ \tfrac{5}{8},\ \tfrac{1}{4}-u,\ \tfrac{1}{2}-u\ :\ \tfrac{1}{8},\ u+\tfrac{1}{4},\ u+\tfrac{1}{2}\ :\ \tfrac{7}{8},\ u+\tfrac{3}{4},\ \bar{u}\ :$$
$$u,\ \tfrac{3}{8},\ \tfrac{3}{4}-u\ :\ \tfrac{1}{2}-u,\ \tfrac{5}{8},\ \tfrac{1}{4}-u\ :\ u+\tfrac{1}{4},\ \tfrac{1}{8},\ u+\tfrac{1}{4}\ :\ \bar{u},\ \tfrac{7}{8},\ u+\tfrac{3}{4}$$

8 atoms.

$$v,\ v,\ v\ :\ v+\tfrac{1}{2},\ \tfrac{1}{2}-v,\ \bar{v}\ :\ \bar{v},\ v+\tfrac{1}{2},\ \tfrac{1}{2}-v\ :\ \tfrac{1}{2}-v,\ \bar{v},\ v+\tfrac{1}{2}\ :$$
$$\tfrac{3}{4}-v,\ \tfrac{3}{4}-v,\ \tfrac{3}{4}-v\ :\ v+\tfrac{1}{4},\ \tfrac{1}{4}-v,\ v+\tfrac{3}{4}\ :\ \tfrac{1}{4}-v,\ v+\tfrac{3}{4},\ v+\tfrac{1}{4}\ :\ v+\tfrac{3}{4},\ v+\tfrac{1}{4},\ \tfrac{1}{4}-v.$$

The choice of values for u and v has now to be made so as to satisfy the observed intensities. The group O_h^7 is characterized by the quartering of the (100) spacing. Reference to the list of observed intensities of the oscillating crystal method shows that no reflexion is observed from any of the first six orders of (100). The utility of the method is here well illustrated, because in the powder method reflexions are observed at the required values of $\sin\theta$ for (300), (500), and

* Phil. Trans. Roy. Soc. A, ccxxiv. p. 225.

† 'Analytical Expression of the Results of the Theory of Space-Groups,' pp. 137, 104 and 105.

(600), but the oscillating crystal method shows that these reflexions are in reality due to the planes (221), (430), and (442) respectively. With the exception of (400) all the reflexions from (100) automatically disappear in this group, so that a choice of u and v must now be made so that (400) also is of small intensity, because this plane has not been observed in either the powder or the oscillating crystal photographs.

The intensity of reflexion from the plane (hkl) is given by

$$\mathrm{I} = k(\mathrm{A}^2+\mathrm{B}^2),$$

where k is a function of the angle of reflexion (θ), and

$$\mathrm{A} = \Sigma \cos 2\pi(hx_s+ky_s+lz_s),$$

$$\mathrm{B} = \Sigma \sin 2\pi(hx_s+ky_s+lz_s),$$

$(x_s\, y_s\, z_s)$ being the coordinates of the atoms in the unit. For the plane (400)

$$\mathrm{A}_{400} = 8\ (\cos 2\pi 4u+\cos 2\pi 4v-\tfrac{1}{2}), \quad \mathrm{B}_{400} = 0.$$

The possible values of u are limited by the fact that the centres of the atoms cannot approach one another too closely. In α-manganese neighbouring atoms are separated by distances varying from 2·24 Å. to 2·96 Å. Since the density of β-manganese is less than that of α-manganese, it is reasonable to assume that the minimum distance of approach of atoms is not less than 2·25 Å. The distance between the atoms $(u, \frac{3}{8}\ \frac{3}{4}-u)$ and $(\frac{1}{8},\ u+\frac{1}{4},\ u+\frac{1}{2})$ is

$$2r = a\,\{2(u-\tfrac{1}{8})^2+(2u-\tfrac{1}{4})^2\}^{1/2} = a(\tfrac{1}{8}-u)\ \sqrt{6},$$

where $a=6{\cdot}29$ Å. When $u=0$, $2r=1{\cdot}93$ Å. and r diminishes as u increases from zero. Consequently, a small negative value of u is required to make $2r$ exceed 2·25 Å. The minimum numerical value of u is about 0·021, giving $2\pi u=-7{\cdot}5°$; the value of $2\pi v$ required to make A_{400} very small is about 28° with this value of u. Consider, now, the intensity of the line (311), which is observed to be fairly intense. For this plane, $\mathrm{B}=-\mathrm{A}$ and the 12 atoms contribute to A a quantity $-3\sqrt{2}\sin 2\pi\,.\,2u$, while the contribution from the 8 atoms to A is

$$\cos 2\pi 5v+2\cos 2\pi 3v+\cos 2\pi v$$

$$-\sin 2\pi 5v+2\sin 2\pi 3v-\sin 2\pi v.$$

The former of these expressions is positive if u is negative, and increases with u; the latter is also positive and increases as v diminishes. Trial showed that the above minimum value of u and maximum value of v gave too small an intensity for (311), so the intensities of all planes have been computed for the following values of u and v chosen to make A_{400} very small :—

	$2\pi u$.	$2\pi v$.
(1)	$-12°$	$25°$
(2)	-16	22
(3)	-20	20

Arrangement (2) gave results definitely in better agreement with observation than either (1) or (3). For instance, both (1) and (3) make A^2+B^2 for (222) too strong in comparison with the value for (320), the former plane being absent from the photographs and (320) giving a weak reflexion. The values of A^2+B^2 for arrangement (2) are given in Table I., column 5, and may be compared directly with the results of the oscillating crystal photographs in column 4. The agreement is very good.

As regards the powder photographs, the observed intensity may be compared with the quantity $N(A^2+B^2)/(h^2+k^2+l^2)$, the values of which are given in column 6 of the table. Here N is the number of planes (hkl) in the crystal. In the seventh column are entered the intensities as given by Westgren and Phragmén. The agreement is again very good, and is even better than comparison of columns 6 and 7 would indicate. For instance, the lines due to Kα radiation for which Σh^2 is 9, 10, and 11, are recorded as "strong" by Westgren and Phragmén, while the Kβ reflexions are recorded as strong, medium, and weak respectively, the order of fall of intensity agreeing with the fall of the calculated values. Again, no reflexion is recorded for the plane 422, which, judging by the calculated values of the neigh bouring lines, should have been weak. There is recorded however, a reflexion (Table 3 of the paper referred to) for which $\sin^2\theta=0{\cdot}800$, so that $\sin^2\theta/24=0{\cdot}03333$ if the reflexion is ascribed to (422) ($\Sigma h^2=24$). For the other Kα reflexions recorded by Westgren and Phragmén, the mean value of $\sin^2\theta/\Sigma h^2$ is $0{\cdot}03331$, so that the α reflexion of (422) coincides with the β reflexion from (432) and (520), and is not separately recorded.

The last three columns contain a comparison between the calculated order of intensity and that observed. For this purpose a powder photograph was taken with iron radiation which was filtered through a screen of manganese oxide (Mn_3O_4) to absorb the Kβ radiation and so diminish the fogging of the film due to scattering. The observed lines have been entered in column 9 of the table in order of intensity, 1 being the most intense and 13 the least. In the eighth column is given the order in which the values of $N(A^2+B^2)/h^2+k^2+l^2$ fall. It will be seen that there is a very general agreement between the two columns. The last line recorded in the table is observed to be stronger than the calculation would indicate, but no allowance has been made in the calculation for the fact that at small and large angles of reflexion the reflected energy is distributed over the surface of a cone of small angle. To make allowance for this, the last column of the table is the order in which the values of

$$\frac{N(A^2+B^2)}{(h^2+k^2+l^2)\sin 2\theta}$$

fall. This alteration has the effect of increasing the calculated figures at the beginning and end of the spectrum, and effects an improvement in agreement between theory and observation in the case of the lines for which Σh^2 is 30 and 41, without affecting the remaining lines appreciably. The agreement is quite as good as is to be expected. It is, perhaps, worth while remarking that the calculated intensity of the most intense line is 272, and of the 7th most intense line is 38·9, while the 14th is 25·3. The most we can expect, then, of a comparison between theory and experiment is that lines 7 to 14 should have about the same intensity, which is, in fact, the case.

The above somewhat lengthy discussion of the intensity of the lines has been rendered necessary by the difficulty of obtaining a single crystal of the material capable of yielding an oscillating crystal photograph that could be relied on, but it leaves little doubt that the structure proposed accounts for the observed intensity of reflexion. A drawing of the unit cube is shown in fig. 2, the numbers attached to the atoms corresponding to those given in Table II., which includes a list of the coordinates of the atoms expressed in degrees, and shows that the groups O^6 and O^7 cannot be distinguished by X-rays although they are physically different, being related

Table II.—Coordinates of Atoms.

O_6.

12*q*. $2\pi u = -16°$.

1	$u+\frac{1}{4}$	$\bar{u}$	$\frac{5}{8}$	74	16	−135
2	$u+\frac{3}{4}$	$u+\frac{1}{2}$	$\frac{3}{8}$	−106	164	135
3	$\frac{3}{4}-u$	$\frac{1}{2}-u$	$\frac{7}{8}$	− 74	−164	− 45
4	$\frac{1}{4}-u$	u	$\frac{1}{8}$	106	− 16	45
5	$\frac{5}{8}$	$u+\frac{1}{4}$	$\bar{u}$	−135	74	16
6	$\frac{3}{8}$	$u+\frac{3}{4}$	$u+\frac{1}{2}$	135	−106	164
7	$\frac{7}{8}$	$\frac{3}{4}-u$	$\frac{1}{2}-u$	− 45	− 74	−164
8	$\frac{1}{8}$	$\frac{1}{4}-u$	u	45	106	− 16
9	$\bar{u}$	$\frac{5}{8}$	$u+\frac{1}{4}$	16	−135	74
10	$u+\frac{1}{2}$	$\frac{3}{8}$	$u+\frac{3}{4}$	164	135	−106
11	$\frac{1}{2}-u$	$\frac{7}{8}$	$\frac{3}{4}-u$	−164	− 45	− 74
12	u	$\frac{1}{8}$	$\frac{1}{4}-u$	− 16	45	106

8*j*. $2\pi v = -22°$.

13	v	v	v	− 22	− 22	− 22
14	$v+\frac{1}{2}$	$\frac{1}{2}-v$	$\bar{v}$	158	−158	22
15	$\bar{v}$	$v+\frac{1}{2}$	$\frac{1}{2}-v$	22	158	−158
16	$\frac{1}{2}-v$	$\bar{v}$	$v+\frac{1}{2}$	−158	22	158
17	$\frac{1}{4}-v$	$\frac{1}{4}-v$	$\frac{1}{4}-v$	112	112	112
18	$v+\frac{3}{4}$	$\frac{3}{4}-v$	$v+\frac{1}{4}$	−112	− 68	68
19	$\frac{3}{4}-v$	$v+\frac{1}{4}$	$v+\frac{3}{4}$	− 68	68	−112
20	$v+\frac{1}{4}$	$v+\frac{3}{4}$	$\frac{3}{4}-v$	68	−112	− 68

O_7.

12*r*. $2\pi u = -16°$.

1	$\frac{3}{4}-u$	u	$\frac{3}{8}$	− 74	− 16	135
2	$\frac{1}{4}-u$	$\frac{1}{2}-u$	$\frac{5}{8}$	106	−164	−135
3	$u+\frac{1}{4}$	$u+\frac{1}{2}$	$\frac{1}{8}$	74	164	45
4	$u+\frac{3}{4}$	$\bar{u}$	$\frac{7}{8}$	−106	16	− 45
5	$\frac{3}{8}$	$\frac{3}{4}-u$	u	135	− 74	− 16
6	$\frac{5}{8}$	$\frac{1}{4}-u$	$\frac{1}{2}-u$	−135	106	−164
7	$\frac{1}{8}$	$u+\frac{1}{4}$	$u+\frac{1}{2}$	45	74	164
8	$\frac{7}{8}$	$u+\frac{3}{4}$	$\bar{u}$	− 45	−106	16
9	u	$\frac{3}{8}$	$\frac{3}{4}-u$	− 16	135	− 74
10	$\frac{1}{2}-u$	$\frac{5}{8}$	$\frac{1}{4}-u$	−164	−135	106
11	$u+\frac{1}{2}$	$\frac{1}{8}$	$u+\frac{1}{4}$	164	45	74
12	$\bar{u}$	$\frac{7}{8}$	$u+\frac{3}{4}$	16	− 45	−106

8*k*. $2\pi v = 22°$.

13	v	v	v	22	22	22
14	$v+\frac{1}{2}$	$\frac{1}{2}-v$	$\bar{v}$	−158	158	− 22
15	$\bar{v}$	$v+\frac{1}{2}$	$\frac{1}{2}-v$	− 22	−158	158
16	$\frac{1}{2}-v$	$\bar{v}$	$v+\frac{1}{2}$	158	− 22	−158
17	$\frac{3}{4}-v$	$\frac{3}{4}-v$	$\frac{3}{4}-v$	−112	−112	−112
18	$v+\frac{1}{4}$	$\frac{1}{4}-v$	$v+\frac{3}{4}$	112	68	− 68
19	$\frac{1}{4}-v$	$v+\frac{3}{4}$	$v+\frac{1}{4}$	68	− 68	112
20	$v+\frac{3}{4}$	$v+\frac{1}{4}$	$\frac{1}{4}+v$	− 68	112	68

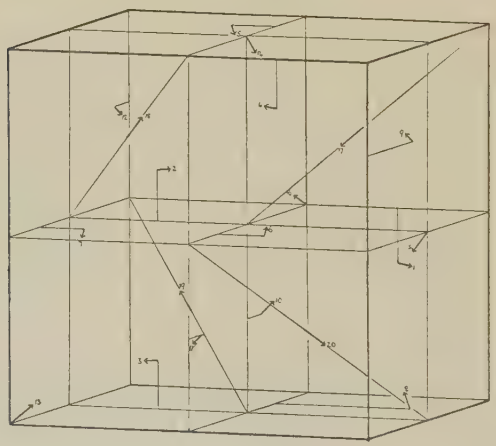
to one another in the same way as an object and its mirror image. Table III. gives a list of the distances between neighbouring atoms.

TABLE III.

Interatomic Distances.

From	To	Å.	From	To	Å.
13	1, 5, 9	2·675	1	13, 17	2·675
13	3, 7, 11	2·671	1	15, 19	2·671
13	4, 8, 12	2,530	1	16, 20	2·530
13	18, 19, 20	2·365	1	6, 11	2·615
			1	7, 8, 10, 12	2·659

Fig. 2.



The Impossibility of Other Atomic Groups.

It has been shown above that an atomic grouping of the type O^7 (or O^6) gives a good account of the observed X-ray spectrum. It remains to be shown that no selection of coordinates for the atoms from the groups T_d^1, O^1, O^2, or O_h^1 can give the observed X-ray spectrum.

The possible positions of atoms in the group T_d^1 are as follows* :—

Equivalent Positions.	Coordinates.				
1	$1(a)$	(ooo)			
	$1(b)$	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$			
3	$3(a)$	$(\frac{1}{2}\frac{1}{2}o)$	$(\frac{1}{2}o\frac{1}{2})$	$(o\frac{1}{2}\frac{1}{2})$	
	$3(b)$	$(\frac{1}{2}oo)$	$(o\frac{1}{2}o)$	$(oo\frac{1}{2})$	
4	$4(a)$	(uuu)	$(u\bar{u}\bar{u})$	$(\bar{u}u\bar{u})$	$(\bar{u}\bar{u}u)$
6	$6(a)$	(uoo)	(ouo)	(oou)	
		$(\bar{u}oo)$	$(o\bar{u}o)$	$(oo\bar{u})$	
	$6(d)$	$(\frac{1}{2}u\frac{1}{2})$	$(\frac{1}{2}\frac{1}{2}u)$	$(u\frac{1}{2}\frac{1}{2})$	
		$(\frac{1}{2}\bar{u}\frac{1}{2})$	$(\frac{1}{2}\frac{1}{2}\bar{u})$	$(\bar{u}\frac{1}{2}\frac{1}{2})$	
12	$12(f)$	$(uo\frac{1}{2})$	$(\bar{u}o\frac{1}{2})$	$(u\frac{1}{2}o)$	$(\bar{u}\frac{1}{2}o)$
		$(\frac{1}{2}uo)$	$(\frac{1}{2}\bar{u}o)$	$(ou\frac{1}{2})$	$(o\bar{u}\frac{1}{2})$
		$(o\frac{1}{2}u)$	$(o\frac{1}{2}\bar{u})$	$(\frac{1}{2}ou)$	$(\frac{1}{2}o\bar{u})$
	$12(g)$	(uuv)	$(u\bar{u}\bar{v})$	$(\bar{u}u\bar{v})$	$(\bar{u}\bar{u}v)$
		(vuu)	$(\bar{v}u\bar{u})$	$(\bar{v}\bar{u}u)$	$(v\bar{u}\bar{u})$
		(uvu)	$(u\bar{v}\bar{u})$	$(\bar{u}\bar{v}u)$	$(\bar{u}v\bar{u})$

The arrangements $1(a)$, $1(b)$, $3(a)$, and $3(b)$ can occur only once in the unit because there are no variable parameters in these arrangements. Subject to the assumption that the centres of atoms must be separated by a distance not less than 2·25 Å., arrangement $4(a)$ may occur three times. It cannot occur five times, and if four groups of $4(a)$ are included in the unit, the remaining four atoms must include one of the arrangements $1(a)$ or $1(b)$, thus placing five atoms on each cube diagonal of length 10·9 Å. The arrangements $6(a)$ can occur only once, because it places two atoms on the side of the cube. A second group of $6(a)$ would thus put four atoms in a length of 6·29 Å. For the same reason $6(d)$ can occur only once. As there are only twenty atoms in the unit, $12(f)$ and $12(g)$ can each occur only once.

Subject to these restrictions there are twenty-six possible ways of putting twenty atoms in the unit. The following scheme shows how these arrangements arise :—

* The notation $1(a)$, $3(a)$, etc., is that used by Wyckoff in 'The Analytical Expression of the Results of the Theory of Space Groups,' and has been retained to facilitate reference to that work.

TABLE IV.

	Number of Atoms.				
	12.	6.	4.	3.	1.
1	*f*	*a*	—	—	*ab*
2	*f*	*d*	—	—	*ab*
3	*f*	—	*aa*	—	—
4	*f*	—	*a*	*a*	*a*
5	*f*	—	*a*	*a*	*b*
6	*f*	—	*a*	*b*	*a*
7	*f*	—	*a*	*b*	*b*
8	*f*	—	—	*ab*	*ab*
9	*g*	*a*	—	—	*ab*
10	*g*	*d*	—	—	*ab*
11	*g*	—	*aa*	—	—
12	*g*	—	*a*	*a*	*a*
13	*g*	—	*a*	*a*	*b*
14	*g*	—	*a*	*b*	*a*
15	*g*	—	*a*	*b*	*b*
16	*g*	—	—	*ab*	*ab*
17	—	*ad*	*aa*	—	—
18	—	*ad*	*a*	*a*	*a*
19	—	*ad*	*a*	*a*	*b*
20	—	*ad*	*a*	*b*	*a*
21	—	*ad*	*a*	*b*	*b*
22	—	*a*	*aaa*	—	*ab*
23	—	*a*	*aa*	*ab*	—
24	—	*d*	*aaa*	—	*ab*
25	—	*d*	*aa*	*ab*	—
26	—	—	*aaa*	*ab*	*ab*

A number of these arrangements may be rejected by considering what pairs of groups place atoms too close together. The arrangements $6(a)$ and $1(a)$ place three atoms on the cube edge of length 6·29 Å., and the arrangements $6(d)$ and $1(b)$ place three atoms in the same length. Both u and $1-2u$ cannot exceed one-third, *i. e.* the interatomic distance must be less than 2·1 Å. contrary to hypothesis. This eliminates arrangements 1, 2, 9, 10, 18, 19, 20, 21, 22, and 24.

The pair of arrangements $6(a)$ and $3(b)$ cannot occur together because the distance from the point (uoo) to $(\frac{1}{2}oo)$ must exceed 2·25 Å., i. e. $u < 0{\cdot}145$, while, if the distance (uoo) to (ouo) is to exceed 2·25 Å., $u > 0{\cdot}25$. The same argument applies to the pair of groups $6(d)$ and $3(a)$. Arrangements 23 and 25 are therefore excluded. Arrangement 26 places five atoms on the cube diagonal which is not possible.

The pair of arrangements $12(f)$ and $3(a)$ is impossible. For the value of u in $12(f)$ is fixed within the limits $0{\cdot}32 > u > 0{\cdot}25$, but if the distance $(\frac{1}{2}\frac{1}{2}o)$ to $(\frac{1}{2}uo)$ is to exceed 2·25 Å., $u < 0{\cdot}145$. Similarly, if the distance $(\frac{1}{2}oo)$ $(\frac{1}{2}uo)$ is to exceed 2·25 Å., $u > 0{\cdot}355$. Accordingly, $12(f)$ cannot occur with either $3(a)$ or $3(b)$, thus eliminating arrangements 4, 5, 6, 7, and 8. So far as consideration of space goes, the remaining groups—namely, 3, 11, 12, 13, 14, 15, 16, and 17—are possible. They must be considered individually to ascertain if they can account for the observed intensities.

Arrangement 3. $12(f)$, $4(a_1)$, $4(a_2)$. — The intensity factor A for the planes *hoo* for this grouping is

$$A_{hoo} = 4(2 + \cos 2\pi uh + \cos 2\pi a_1 h + \cos 2\pi a_2 h),$$

and the B term vanishes. Now the parameter u fixing the position of the atoms $12(f)$ must lie between 0·32 and 0·25, *i. e.* $115° > 2\pi u > 90°$; the parameter $2\pi a_1$ must exceed 45°, while a_2 may be about 135°, −45°, or −135°. For the fourth order reflexion to be small we must have $2\pi u = 115°$, $2\pi a_1 = 45°$, $2\pi a_2 = -45°$ or $+135°$. The values of A for the first six orders of *hoo* are then

	A. $2\pi a_3 = 45.$	A. $2\pi a_2 = 135.$
100	11·9	6·3
200	5·4	5·4
300	6·2	11·8
400	−0·7	−0·7
500	−0·9	4·7
600	11·5	11·5

As no reflexion from any of the first six orders of (hoo) is observed, this arrangement is impossible.

Arrangements 11 to 16 all include the group $12(g)$, the contribution from which to the intensity term of $(h00)$ is

$$A = 4(2\cos 2\pi uh + \cos 2\pi vh) \quad \text{and} \quad B = 0.$$

Consideration of the distance between (uuv) and $(\bar{u}uv)$ shows that $u > 0{\cdot}125$, and of the distance between (uuv) and $(1-u, 1-u, v)$ that $u < 0{\cdot}378$. Hence $135° > 2\pi v > 45°$. Also $u-v > 0{\cdot}251$ from consideration of the distance (uuv) to (uvu), or $2\pi u - 2\pi v > 90°$, u and v being both positive and less than $0{\cdot}5$. Table V. shows the value of $2\cos 2\pi uh$ for different values of u within these limits, and for values of h from one to six.

TABLE V.

	$u = 50$	60	70	80	90	100	110	120	130
1 ...	1·28	1·0	0·68	0·35	0	−0·35	−0·68	−1·0	−1·28
2 ...	−0·35	−1·0	−1·53	−1·88	−2·0	−1·88	−1·53	−1·0	−0·35
3 ...	−1·73	−2·0	−1·73	−1·0	0	1·0	1·73	2·0	1·73
4 ...	−1·88	−1·0	0·35	1·53	2·0	1·5	0·35	−1·0	−1·88
5 ...	−0·68	1·0	1·97	1·53	0	−1·5	−1·97	−1·0	0·68
6 ...	1·0	2·0	1·0	−1·0	−2·0	−1·0	1·0	2·0	1·0

Arrangement 11. $12(g)$, $4(a_1)$, $4(a_2)$.—The values of $2\pi a_1$, $2\pi a_2$ are between 45° and 135°, so that the contribution of these eight atoms to A_{200} is always negative or zero. From the table it is seen that the value of $2\cos 2\pi uh$ is also negative or zero when $h=2$. To make the intensity of 200 small we must have a_1 and a_2 approximately 45° or 135°, and then either $45° < u < 60°$ and $145° < v < 180°$, or $120° < u < 135°$ and $0° < v < 35°$. Considering now the case of (100), it seems that we must put $a_1=45$ and $a_2=135$. A for 100 and 200 will now be small, but the contribution of every term except $\cos 2\pi vh$ is negative for (400) and is positive for (600). This arrangement is, therefore, impossible.

Arrangement 12. $12(g)$, $4(a)$, $3(a)$, $1(a)$.—The contribution to A_{h00} from the atoms $1(a)$ and $3(a)$ is $2(1+\cos \pi h)=4$ or 0, according as h is even or odd. We now have :

$$A_{h00} = 4(2\cos 2\pi uh + \cos 2\pi vh + \cos 2\pi ah) + 2(1+\cos \pi h),$$

where $2\pi a$ lies between 45° and 135°, and $2\pi u$ is now confined within the limits $50° < u < 90°$, the corresponding limits of $2\pi v$ being $140° < v < 180°$. The values of A for (hho) and (hhh) are

$$A_{hho} = 4(\cos^2 2\pi uh + 2\cos 2\pi uh \cos 2\pi vh + \cos^2 2\pi ah) + 2(1+\cos \pi h),$$

$$A_{hhh} = 12\cos^2 2\pi uh \cos 2\pi vh + 4\cos^3 2\pi ah + 4.$$

Now, when $h=2$, $\cos 2\pi vh$ is positive; so to make A_{222} small, we must put $a=20$ and $u=50$, with $140° < v < 180°$, which makes A_{220} quite large, and is otherwise inconsistent with the observed intensities.

The expression A_{hho} and A_{hhh} for the arrangements 13, 14, and 15 are the same as those for arrangement 11, so that these groups are also impossible.

Arrangement 16. $12(g), 3(a), 3(b), 1(a), 1(b)$.—The values of A are now

$$A_{hoo} = 4(2\cos 2\pi uh + \cos 2\pi vh) + 4(1+\cos \pi h),$$

$$A_{hho} = 4(\cos^2 2\pi uh + 2\cos 2\pi uh \cos 2\pi vh) + 4(1+\cos \pi h),$$

$$A_{hhh} = 12\cos^2 2\pi uh \cos 2\pi vh + 4(1+\cos \pi h).$$

In order that A_{111} may be small, $2\pi u = 90°$, and therefore $2\pi v = 0°$ or 180°; but this makes A_{400} very large and also places the atoms too close together, and is, therefore, impossible.

Arrangement 17. $6(a)$, $6(d)$, $4(a_1)$, $4(a_2)$.—The parameter a, fixing the position of the atoms $6(a)$, lies within the limits $115° > 2\pi a > 90°$; while d, fixing $6(d)$, lies within $90° > 2\pi d > 64°$. The only possible arrangement of $4(a_1)$ and $4(a_2)$ is $2\pi a_1 = 90°$ and $2\pi a_2 = -90°$, with $2\pi a = 134°$ and $2\pi d = 65°$. Even now the atom centres come slightly within the limits we have supposed possible. But in any case, we have

$$A_{hoo} = 2(2+\cos 2\pi ah) + 2(2\cos \pi h + \cos 2\pi dh) + 4\cos 2\pi a_1 h + 4\cos 2\pi a_2 h,$$

which is large when $h=4$ and $2\pi a_1$, $2\pi a_2$ are nearly 90°. The arrangement is, therefore, impossible.

There is, then, no combination of positions for atoms in the group T_d^1 which can account for the observed X-ray spectrum and at the same time keep the distance between atoms in excess 2·25 A.

O^1.

The possible positions of atoms in this group are :

$1(a)$ $1(b)$

$3(a)$ $3(b)$

$6(a)$ $6(d)$

$6(b)$ $(\frac{1}{2}uo)$ $(o\frac{1}{2}u)$ $(uo\frac{1}{2})$

$(\frac{1}{2}\bar{u}o)$ $(o\frac{1}{2}\bar{u})$ $(\bar{u}o\frac{1}{2})$

$6(c)$ $(ou\frac{1}{2})$ $(\frac{1}{2}ou)$ $(u\frac{1}{2}o)$

$(ou\frac{1}{2})$ $(\frac{1}{2}ou)$ $(o\frac{1}{2}u)$

$8(c) = 4(a)$ and $4(-a)$

$12(m) = 12(g)$ with $v = o$

$12(n) = 12(g)$ with $v = \frac{1}{2}$

The only new cases arising are those involving $6(b)$ and $6(c)$. Neither of these groups can be combined with either $3(a)$ or $3(b)$, so the only new series are: (1) $6(b)$, $6(c)$, $8(c)$, which is very similar to arrangement 3 of Table IV.; (2) $6(a)$, $6(b)$, $8(c)$; and (3) $6(d)$, $6(b)$, $8(c)$. In the first of these new arrangements, the parameters b and c defining the positions of the atoms $6(b)$ and $6(c)$ must lie between 65° and 115°, and if $b > 90°$, $c < 90°$. Consideration of the fourth order of (100) necessitates $b = 66°$, $c = 114°$, and $c^1 = 45°$ (or 135) when c^1 defines the positions $8(c)$. But this arrangement makes (200) and (300) too strong. Similar arguments exclude the remaining two cases.

O^2.

The possible positions are as follows:—

$2(a) = 1(a)$ and $1(b)$

$4(d) = 4(a)$ with $a = \frac{1}{4}$

$4(e) = 4(a)$ with $a = \frac{3}{4}$

$6(e) = 3(a)$ and $3(b)$

$6(f) = 6(b)$ with $b = \frac{1}{4}$

$6(g) = 6(c)$ with $c = \frac{1}{4}$

$8(d) = 4(a)$ and $4(a_2)$ $a_2 = \frac{1}{2} - a$

$12(a) = 6(a)$ with $6(d)$ $d = a + \frac{1}{2}$

$12(i) = 6(b)$ with $6(b_2)$ $b_2 = b_1 + \frac{1}{2}$

$12(j) = 6(c_1)$ with $6(c_2)$ $c_2 = c_1 + \frac{1}{2}$

$11(o)$ and $12(p)$

The only new cases are those involving $12(o)$ and $12(p)$. The coordinates of the equivalent positions $12(o)$ are :

$$\begin{array}{llll}
(u \quad \tfrac{1}{2}-u \quad \tfrac{1}{4}) & (u \quad u+\tfrac{1}{2} \quad \tfrac{3}{4}) & (\bar{u} \quad \tfrac{1}{2}-u \quad \tfrac{3}{4}) & (\bar{u} \quad u+\tfrac{1}{2} \quad \tfrac{1}{4}) \\
(\tfrac{1}{4} \quad u \quad \tfrac{1}{2}-u) & (\tfrac{3}{4} \quad u \quad u+\tfrac{1}{2}) & (\tfrac{3}{4} \quad \bar{u} \quad \tfrac{1}{2}-u) & (\tfrac{1}{4} \quad \bar{u} \quad u+\tfrac{1}{2}) \\
(\tfrac{1}{2}-u \quad \tfrac{1}{4} \quad u) & (u+\tfrac{1}{2} \quad \tfrac{3}{4} \quad u) & (\tfrac{1}{2}-u \quad \tfrac{3}{4} \quad \bar{u}) & (u+\tfrac{1}{2} \quad \tfrac{1}{4} \quad \bar{u})
\end{array}$$

The contribution to A_{hoo} from these atoms is

$$A^{\delta}_{hoo} = 4\cos\frac{\pi h}{2} + \cos 2\pi uh(1+\cos\pi h).$$

Consideration of space shows that $2\pi u$ lies between 0° and 36°. The possible combinations of $6(e)$, $6(f)$, or $6(g)$ with $2(a)$ to give eight more atoms, all contribute 8 units to A_{400}. With $u < 36$, A_{400} is too large. The only possible arrangement is $12(o)$ with $8(d)$ or with $4(d)$ and $4(e)$. The latter will make A_{400} large. With the former arrangement the values $2\pi u = 15°$, $2\pi d = 45°$ make $A_{400}=0$ and A_{200} small but not small enough. A_{600} is also too large. With these values of u and d, however, $A_{222}=-9$, which is much too large. This arrangement is therefore, not possible, and $12(p)$ leads to a similar result.

O^1_h.

This group contains no case which has not already been examined and rejected.

There are, therefore, no possible arrangements in any of the groups T^1_d, O^1, O^2, or O^1_h. The crystal must belong to O^6 or O^7, and the only possible arrangement is that already described.

Summary.

The β-modification of manganese stable above 742° C. has been examined at room temperatures by the Laue oscillating crystal and powder methods. The results show that the material crystallizes in the cubic system O^7 (or O^6), the unit having a side of 6·29 Å. and containing 20 atoms. The groups O^6 and O^7 are enantiomorphous and indistinguishable by X-ray methods. It is also shown that these two groups are the only possible ones which can account for the observed intensities of reflexion.

I am indebted to Dr. Marie L. V. Gayler for supplying the material for X-ray examination, and to Dr. W. Rosenhain, F.R.S., for his interest in the work.

CXXVI. *Tesla Luminescence Spectra of the Halogens.*—Part I. *Iodine.* *By* S. S. Bhatnagar, *D.Sc.*, D. L. Shrivastava, *M.Sc.*, K. N. Mathur, *M.Sc.*, *and* R. K. Sharma, *M.Sc.**

[Plate XXI.]

IODINE and bromine have been examined spectroscopically by many investigators. As early as 1898 Konen [1] examined the emission spectra, and gave the positions of several bands and lines in both the visible and the ultra-violet region. The fluorescence spectra have been largely investigated by Wood [2], and later by McLennan [3] and by Oldenburg [4]. Much of the work on the emission spectra has been stimulated by the discovery by Steubing [5], in the case of iodine, of a region of continuous emission ending sharply on the long wave-length side at 4800 ± 15 Å. and its explanation by Franck [6] on the basis of the electron affinity of the halogen. Recent work by Gerlach and Gromann [7], Noyes [8], Ludlam and West [9], Mecke [10], Cario and Oldenburg [11] and others has been mainly directed towards the elucidation of this view.

Attention has been called by several experimenters [12],[13],[14] to differences that occur in emission spectra as a result of the form of excitation. McVicker, Marsh, and Stewart [13] working with organic vapours have found remarkable differences with Tesla frequencies. Swindler [15], working with chlorine and other gases, has found that at low pressures the high-frequency spectra differ widely from 60-cycle spectra with gases containing nitrogen as an impurity. Bloch and Bloch [16], employing high-frequency oscillatory discharge, have been able to obtain several successive stages of ionization. In the present investigation, iodine and bromine have been studied under a high-frequency discharge from the secondary of a Tesla coil excited by a powerful 50-cycle A.C. transformer. In order to avoid all complications due to the presence of electrodes, the discharge was made electrodeless, and to obtain an intense discharge a scheme of connexions rather different from that employed by previous workers was adopted after making a number of trials. The arrangement of McVicker, Marsh, and Stewart [13] consisted in connecting the internal electrode of their discharge-tube to the secondary of an air-insulated

* Communicated by the Authors.

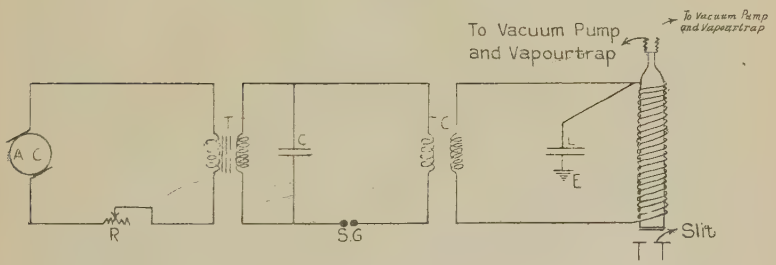
Tesla coil having a directly-coupled primary and using four big Leyden jars, an 18-inch induction coil being used as the source of current. The other electrode, which consisted of tin-foil coating over the entire length of the tube, was earthed along with the other end of the Tesla secondary.

Robertson [17] caused electrodeless discharge in a bulb 12 cm. in diameter by suspending it inside a coil of a few turns of stout copper wire, which was connected to two Leyden jars excited by a transformer.

Experimental.

The arrangement adopted by the authors is shown in fig. 1. Current from a 50-cycle A.C. generator coupled to a D.C. motor was fed to the primary of a dental X-ray

Fig. 1.



transformer T made by the General Electric Company [18] of America, through a regulating rheostat R. The secondary of this was connected to the primary of the Tesla coil TC with a condenser C and a spark-gap as shown. The secondary of the Tesla coil was connected to a solenoid wound on the discharge-tube. The Tesla coil used was made in the laboratory, and had 14 turns of stout bare copper wire for the primary. The secondary had a single layer of 155 turns of 22 S.W.G. D.C.C. wire wound on a thin ebonite former. The space between the ebonite former and the primary coils was filled with paraffin-wax. This gave a fairly tight coupling for the high-frequency circuit. The spark-gap consisted of two adjustable brass knobs 1·3 cm. in diameter. The condenser C was made up of four thin zinc plates of 20×15 cm., with a projection on one side for connexions, separated by 0·6 cm. thick plate glass, size 30×25 cm. Previous to making up, the glass

plates were cleaned and thoroughly dried. The whole of the block was then set in good paraffin-wax. The capacity of this condenser was thus about 370 cm. During the course of preliminary investigation we employed Leyden jars as used by McVicker, Marsh, and Stewart (*loc. cit.*), but we found them very unsatisfactory with long hours of continuous working. Similarly we had also tried two other forms of Tesla coil. One had a primary of four turns over a long secondary of about a thousand turns or more, the two being air-spaced; the other was simply made by connecting together the two ends of the solenoid over the discharge-tube and winding over it a few turns of copper wire separated by a large air-distance and connected to the Tesla secondary. In both these cases the intensity of discharge becomes very feeble. The air-spaced coupling cannot work satisfactorily, because at the high potential employed there is always a vigorous corona discharge.

The discharge-tube used by us consisted of a glass tubing 2·5 cm. in diameter and 30 cm. long. One end was finely ground so that a quartz plate (as supplied by Adam Hilger Ltd. for Baly absorption-tube) could be cemented on it. The other end was drawn out and suitably narrowed for taking a joint of thick rubber tubing. The whole of the tube, excepting about 2 cm. from either end, was wound over with 250 turns of insulated 22 S.W.G. copper wire, which was well varnished with shellac. The two ends of this solenoid were joined to the secondary of the Tesla coil. One of these ends was also joined to the knob of a Leyden jar whose outer coating was earthed. This considerably increased the intensity of discharge, due no doubt to the capacity putting this circuit in better tuning with the primary oscillating circuit of the Tesla.

A wash-bottle filled with suitable absorbing substances was included between the discharge-tube and the vacuum pump to catch the halogen vapours. A Cenco Hyvac pump was used for exhausting. The instrument used for photographing the spectra was a quartz spectrograph, size E 3, made by Adam Hilger Ltd. It gives a spectrum about 200 mm. in length between λ 2100 and 7000 Å. The wave-lengths were measured by the scale mounted in the instrument. This scale was further standardised by comparing it with standard copper lines. The error of reading, as shown by our copper spectrum, is 1 Å. for λ 2200, increasing to about 10 Å. for λ 7000. Wellington Spectrum plates were used throughout and found very suitable, both as regards the speed and freedom from halation. The

maker's metol-hydroquinone formula was adopted for development.

Iodine.

Merck's extra pure resublimed iodine was carefully resublimed again, and the sample thus obtained was used for the experiments. A sufficient quantity of the crystals was then spread throughout the length of the discharge-tube. The quartz window was then cemented, using Everett's hard vacuum wax, and connexion was made with the vacuum pump through an absorption-trap. At a pressure of 3 mm. the discharge has a beautiful bluish glow throughout the entire length of the tube. An exposure of half-an-hour was found sufficient with the discharge-tube about 3 cm. from the spectrograph slit.

Results.

An examination of the iodine spectrum shows the following peculiarities :—

(*a*) A continuous background beginning from λ 4800 and ending at λ 2130. Both the edges at λ 4800 and λ 2130 are sharp.

(*b*) A number of emission bands superposed on the continuous background.

(*c*) A few of the iodine emission lines. These are visible only outside the region of continuous emission.

(*d*) An almost complete absorption of radiation in the region λ 4800 to λ 5650.

A narrow continuous background with its maximum wave-length limit at λ 4800 was first observed by Steubing [5]. The extension of the continuous emission up to λ 2130 has not been previously observed.

The emission bands (*b*) with their positions are given on p. 1232. Some of these bands have been previously located, but we have been able to note many new bands further in the ultra-violet.

Wood and Kimura [19] give a long list of closely-spaced iodine lines between λ 4632 and λ 6585. Of these, Pl. XXI. shows λλ 4835, 4865, 5200, 5650, 6200, 6450 only. These coincide with their lines within the accuracy of our readings. Wood and Kimura were able to change gradually from band to line spectra by varying the capacity in the circuit or by heating. They were thus led to conclude that the line spectrum is due to the atoms, and that the dissociation of the iodine molecule results from an elevation of temperature.

St. Landau-Ziemecki [20], applying a formula of Bodenstein and Stark [21], calculates that at 500° C. and 1/4 mm. pressure the degree of dissociation of iodine molecule is 0·1. In our experiments the pressure was 3 mm., and the rise of temperature, even with prolonged exposures, could not be appreciably higher than 25° C. The degree of dissociation should thus be of the order of 10^{-11}. This is evidently too small a dissociation to show any of the lines ascribed to atomic iodine. We thus think that in our tube the discharge itself was responsible for the dissociation of the molecular into atomic iodine, irrespective of temperature. This accords with Franck's [22] view that the halogens belong to the class of molecules that are able to take up so much oscillation energy through absorption that they dissociate into a normal and an excited atom.

Wood and Kimura have also observed the spectrum of electrically-excited iodine vapour as being made up of a fluted band spectrum between wave-lengths λ 5200 and λ 7000 and a continuous band between wave-lengths 4300 and 4800 Å. The former has been shown by them to exhibit, under high dispersion, a structure comparable to that of the absorption spectrum. In our plate we find an almost complete absorption of radiations (with the exception of three atomic lines mentioned above) between the wave-lengths λ 4800 and λ 5650. Mecke [10] has investigated the band-absorption spectra of iodine. His results show a long series of absorption bands stretching in the direction of short wave-lengths and having a real convergence limit at λ 5000, followed by a region of strong continuous absorption. The band limit λ 5000 has been taken by Franck [22] to represent the energy absorbed by a molecule for dissociation and the excitation of one of its atoms. The absence of any radiation in our plate between λ 4800 and λ 5650 is undoubtedly due to the fact that, as the coils in our discharge-tube were not wound completely up to the end of the tube facing the slit, the region (about 2 cm. long), which was only under a weak stimulus, acted as the absorbing layer for all the bands to be found within this spectral region.

We give below tables of the bands systems observed by us. The stronger of these had been previously observed chiefly by St. Landau Ziemecki. We have here the band system starting from λ 4800 and going up to λ 2130, with a continuous background throughout. The most prominent of these bands are those stretching between λλ 4300–4170, λλ 3440–3360 [25], and λλ 2640–2600.

An examination of the bands shows three well-defined and one weak systems. These have their heads approximately at

(A) λ 4320,
(B) λ 3440,
(C) λ 2710,
(D) λ 2481.

The system A is made of a number of very intense but diffuse bands. These are given in Table I. below :—

Table I.

Long wave-length. Edge of bands.	Short wave-length. Edge of bands.	Wave-number for long wave-length edge.
4320·0	4169·0	23148
4096·3	4014·8	24414
3994·2	3933·3	25037
3890·0	3850·0	25707
3812·0	3780·0	26232
3749·0	3720·0	26673
3685·0	3670·0	27137
3640·0	3610·0	27470
3598·0	3569·0	27793
3540·0	—	28248

Owing to their diffuseness and low dispersion of the quartz spectrograph in this region, it has not been possible to find any regularity in these so far.

There are a few bands between λ 4800 and λ 4320 which do not seem to belong to any of these systems. Their long wave-length edges are situated at λ 4750, λ 4680, λ 4610, λ 4480, λ 4390 (line).

The system B consists of a large number of bands, systematically placed and having a very peculiar intensity distribution.

The heads of these bands are given within the limits of our accuracy of reading by a formula of the usual electronic band type,

$$\nu = 29078 + (710n' - 8n'^2) - (213{\cdot}7n'' - {\cdot}6n''^2),$$

where, adopting the accepted notation, n' refers to the

initial electronic state of the emission process and n'' to the final state, and $\nu_0 = 29078$ is the head of the first band with $\Delta n = 0$.

In Table II. below we give the observed wave-numbers and those calculated by the formula. Again the diffuseness of the bands forbids precise measurements; but within these limitations the agreement is perfect.

TABLE II.

Wave-length limits of bands. Å.	Estimated intensity.	Wave-number of head. Observed.	Calculated.	Values of vibrational quantum number. n', n''.
3480	1	28735	28727	1, 5
3440—3360	10	29070	29078	0, 0
			29567	1, 1
3307	2	30239	30253	2, 1
3283—3070	5	30460	30466	2, 0
			30500	3, 3
3258—3243	8	30694	30711	3, 2
3237—3218	8	30893	30923	3, 1
			30945	4, 4
3214—3197	8	31114	31136	3, 0
			31154	4, 3
3190—3176	8	31348	31365	4, 2
3168—3160	3	31566	31577	4, 1
			31583	5, 4
3144—3140	3	31807	31790	4, 0
			31792	5, 3
3124—3113	8	32010	32003	5, 2
3108—3093	7	32175	32205	6, 4
			32215	5, 1
3085—3080	1	32415	32414	6, 3
			32428	5, 0
3066—3051	6	32616	32602	7, 5
			32625	6, 2
3046—3033	7	32830	32811	7, 4
			32837	6, 1
3024—3020	1	33069	33050	6, 0
			33020	7, 3
3008—2995	6	33245	33231	7, 2
2989—2981	7	33456	33443	7, 1
2972—2968	1	33647	33656	7, 0
			33610	8, 3
2958—2944	7	33807	33821	8, 2
			33789	9, 5
2938	2	34037	34033	8, 1
2920	0	34246	34246	8, 0
2908	2	34388	34395	9, 2

TABLE II. (*cont.*).

Wave-length limits of bands. Å.	Estimated intensity.	Wave-number of head. Observed.	Wave-number of head. Calculated.	Values of vibrational quantum number. n', n''.
2880—2863	5	34698	34607	9, 1
			34742	10, 3
			34840	9, 0
2850—2842	3	35087	34953	10, 2
			35165	10, 1
2827—2813	3	35373	35378	10, 0
			35495	11, 2
2798—2790	0	35740	35707	11, 1
			35811	12, 3
2770—2760	1	36023	36021	12, 2
2748	1	36390	36232	12, 1
			36320	13, 3
2739	1	36509	36531	13, 2
2728	1	36657	36743	13, 1

The values calculated above are only for the heads of the various vibrational bands. Each of these bands has a definite thickness due to the associated rotational levels.

In the above analysis it will be seen that large values of n' are the most favoured ones. This was, indeed, anticipated by Franck from the peculiar intensity distribution of the fluorescence spectrum.

The wave-lengths of the systems (C) and (D) are given in Tables III. and IV. respectively.

TABLE III.

Long wave-length. Edge of the bands.	Wave-numbers.	Estimated intensity.
2729	36643	0
2709	36913	2
2693	37133	2
2683	37271	2
2672	37425	0
2601	38446	1 (very diffuse)
2590	38610	1
2582	38729	1
2565	38982	0
2555	39138	0
2532	39494	1

Table IV.

Long wave-length. Edge of the bands.	Wave-numbers.	Estimated intensity.
2480	40322	2 b. d.
2462	40617	0
2450	40816	0
2430	41151	0
2410	41493	0
2390	41841	1 b. d.
2350	42553	1 b. d.
2328	42964	0
2306	43365	0

Most of the bands of Table III. have the appearance of thick lines, except one very diffuse band. The general character of bands in Table IV. is very hazy. All of these are of very low visibility against a continuous background, which made readings very difficult and uncertain. The bands indicated by letters b. d. are very broad and diffuse. The system (D) might be stretching a little further than λ 2306, but it is not possible to locate bands any further. The continuous background, however, extends up to λ 2130, as indicated before.

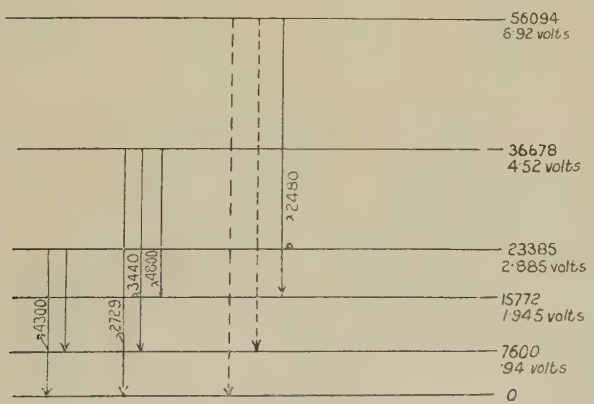
Discussion.

All the heads of the band systems observed by us can be represented within the limits of our accuracy by an energy-level diagram as shown in fig. 2. The numbers on the right-hand side indicate the various term values with equivalent values in volts written below. It will be seen that the first excited state of the molecule differs from the stable state by 0·94 volt. This is the same as the value found by Turner [24] by measuring the recurring doublet separation of the iodine spectrum in the far ultra-violet region. These are the stable and the meta-stable states of the iodine atom, and were first indicated by Franck [22] as $2p_2$ and $2p_1$ states. The level above the $2p_1$ state is 1·005 volt higher, while the next higher is again 0·94 volt higher. It seems here as if the $2p_2$ and $2p_1$ states have undergone a repetition. This is followed by two levels still higher at 4·52 and 6·92 volts respectively. It is significant that transitions from the latter level to the stable and the

meta-stable states gives us two prominent lines of the atomic spectrum of iodine. These are indicated in our diagram by broken lines, and the values of these have been taken from Turner's measurements.

Thus, of our bands the system A is indicated as a transsition from 2·885 volts to the normal state, and the system B as a transition from 4·52 volts to the meta-stable $2p_1$ state, while a transition from this same level to the stable $2p_2$ state gives us the system C. The system D is given by a transition from 6·92 volts to 1·945 volts level. Transitions from this same level to the $2p_2$ and $2p_1$ states gives the two atomic lines of iodine. Besides the above four systems a

Fig. 2.



transition from 4·52 volts to 1·945 volts gives us the edge λ 4800.

It is noteworthy that the line at λ 2062 has been noted by Turner and others as more intense than λ 1876 line. From our diagram it would appear that the latter is the real resonance line. This is also the view of Turner and Compton[25], who regarded λ 2062 as the line terminating on a level 0·545 volt above the normal. Our evidence indicates that it terminates on a 0·94 volt level. The greater intensity of λ 2062 will then mean that the probability of a change, 6·92→0·94 volt, is much greater than 6·92→0 : that is, the atom first tends to assume the meta-stable rather than the stable orbit. This will also explain the greater intensity of the band system B (4·52→·94) over the system C (4·52→0). But this will not explain the great intensity of system A. Indeed, our only justification for creating the level 2·885

has been the peculiar wide separation of the bands most unlike the systems associated with $2p_1$ level. Similarly the edge at λ4800 which on our diagram is associated with the excited levels 4·52—→1·945 defies complete explanation. Gerlach and Gromann[7] have shown that at higher temperatures and lower pressures the band at λ4800 decreases in intensity while that at λ3440 increases in intensity. As these conditions will favour a greater proportion of iodine vapour in the atomic state, they will also, we might suppose, favour the meta-stable state. Thus, clearly the chances for transitions to the $2p_1$ state will be much increased, and consequently the intensity of the band at λ3440[26]. If, however, we follow the same argument for λ4800, we find that, as its terms are higher still, it should also be strengthened. A way of escape from this difficulty is found if we assume that the transitions responsible for λ3440 are possible both in the atomic as well as the molecular state, while those responsible for λ4800 are possible only for the molecular state, and are forbidden on the selection principle in the atomic state. Franck has pointed out that for homopolar molecules like I_2, which are bound together by van der Waals's forces, the electron orbits of the individual atoms still exist, though in a more or less disturbed state. Such molecules can be separated adiabatically into normal atoms, and on excitation by light an electron of one of the atoms passes to a higher quantum orbit, and the corresponding absorption frequency will be almost identical with a frequency found in the spectrum of the constituent atom. Now, several investigators have called attention to the appearance of "forbidden" lines in the molecular spectra. We might thus be justified in assuming that the transitions responsible for λ4800 are only possible in the molecular state, and thus under those conditions of temperature and pressure which favour a greater amount of atomic iodine this band must be necessarily weakened, while that at λ3440 is strengthened. But this does not explain the observations of Steubing and others that even under large dispersion it remains unresolved.

It should be pointed out here that the bands λ4800 and λ3440 are the so-called electron-affinity spectra of iodine. Franck suggested the former while Gerlach and Gromann, Ludlam and West, and others have been leading evidence in favour of the latter. If such a spectrum exists at all for iodine, we would agree with Gerlach[27] and attribute λ4800 to the affinity of the iodine molecule.

Referring to our analysis of the band system B involving a number of vibrational levels associated with the electronic

levels 4·52 and 0·94 volts, it will be seen that the final term of the formula

$$\nu = 29078 + (710n' - 8n'^2) - (213{\cdot}7n'' - {\cdot}6n''^2)$$

is the same as given by Kratzer and Sudholt[28] and corrected by Kemble and Witmer[29] from analysis of the resonance series of iodine. The presence of this term shows that in the above transitions the final state of the molecule is that of the excited $2p_1$ condition. That is, contrary to the usual belief that the vibrational levels of the resonance spectra $(213{\cdot}7n'' - {\cdot}6n''^2)$ are associated with the unexcited normal molecule, we find that even in fluorescence the final level of the emission process is the excited $2p_1$. We also notice that in the system B for all those transitions for which the final vibrational quantum number $n''=0$, the observed bands are very much feebler. That is as it should be, for, as pointed out before, the end of our discharge-tube facing the slit was under a comparatively feeble stimulus, and consequently must necessarily have a great preponderance of molecules in the excited $2p_1$ state. These will act as a partially absorbing layer for all the transitions involving $n''=0$.

On our energy-level diagram the highest value of the electronic energy absorbed by the molecule before it dissociates is $(6{\cdot}92 - 1{\cdot}94) = 4{\cdot}98$ volts. If, now, the molecule dissociates, it will absorb the energy necessary for its dissociation, the rest being evolved as a quantum of light. Referring again to the band at λ 3440, it will be noticed that its great intensity and breadth is not wholly explained by its being the head of the system. The most intense part of this lies at λ 3410, and we consider that this is due to the light-quantum evolved on dissociation of the molecule. Thus, since λ 3410 is equal to 3·62 volts, the energy required for the dissociation of the molecule would be

$$4{\cdot}98 - 3{\cdot}62 = 1{\cdot}36 \text{ volts.}$$

This is slightly lower than the chemically-calculated value 1·5 volts, but is in excellent agreement with the value of Foote and Mohler[30]. The former workers have found a resonance potential in iodine vapour at $2{\cdot}34 \pm 0{\cdot}2$ volts. If from this we subtract 0·94 volt as the energy required for exciting one of the atoms to the meta-stable state, we get the value $1{\cdot}40 \pm 0{\cdot}2$ volts, which agrees with our value within the limits of the accuracy.

Following, again, the contention of Franck and Dymond[31] that the result of the dissociation of iodine when produced by light-absorption is one stable atom and one meta-stable

atom, if we take the excited molecule at 4·98 volts to dissociate as above, the energy absorbed would be

$$1{\cdot}36 + {\cdot}94 = 2{\cdot}30 \text{ volts},$$

and the emitted light-quantum should have the value

$$4{\cdot}98 - 2{\cdot}30 = 2{\cdot}68 \text{ volts}.$$

We should expect a band terminating in this region. We have actually a fairly intense band from λλ 4610–4550. This agrees well.

As already pointed out, the continuous spectrum from λλ 4800–2130 forms a strong background throughout. This seems to be a continuation of the narrow continuous spectrum at λ 4800 of Steubing[5]. An explanation of this will probably be a special case of the general theory of retardation spectra, which is as yet very little understood. For the present, however, we might adopt the views of Wright[32] and of Crew and Hulburt[33] in conjunction with the idea of electron affinity.

Franck, in explaining Steubing's results, conceived the idea of electron affinity spectra as being due to the capture of an electron by the iodine atom because of the tendency of the latter to form a stable octet in its outermost shell. Thus

$$W_i - W_f = h\nu_0,$$

where W_i = energy in the initial state and W_f in the final state and ν_0 the wave-number of emitted quantum, would give the position of the edge ; but since initially the captured electron might possess any velocity, this sharp edge would be followed by a continuous spectrum, that is

$$h\nu = W_i - W_f + \tfrac{1}{2}mv^2 = h\nu_0 + \tfrac{1}{2}mv^2.$$

ν_1 will thus depend on v, the velocity with which the captured electron was moving. It is clear, however, that this velocity cannot be large, for then the electron will penetrate the atom and escape. If, now, the atom (or the molecule in the case of homopolar compounds like iodine, where the atoms more or less maintain their separate entity) is already in an excited state when the electron is captured, then along with molecular bands we should find associated a continuous spectrum. That is, in the above equation each excited quantized state of value W_i giving a band head will also form the head of a continuous spectrum linked up with it. The sharp high-frequency edge at λ 2130 will then mean the maximum velocity $v_{max.}$ of the electrons which can be captured by molecular iodine. With a greater value of any

of these, either the molecule dissociates or the electron escapes. A similar edge, but at λ 2125, is shown by bromine.

Summary.

Iodine has been examined spectroscopically by excitation under electrodeless Tesla discharge. The spectrum obtained has a bright continuous background from λ 4800 to λ 2130 with a number of electronic emission bands superposed on it. Four different systems of bands have been located. One of these systems has been analysed and shown to confirm to the equation

$$\nu = 29078 + (710n' - 8n'^2) - (213{\cdot}7n'' - 0{\cdot}6n''^2),$$

where 29078 is the wave-number of the head of the system. The presence of the fluorescence term $(213{\cdot}7n'' - 0{\cdot}6n''^2)$ has been shown to indicate that this system is given in emission as the molecule returns from a higher excited state to the meta-stable $2p_1$ state. A brief discussion is given of the bands at λ 4800 and λ 3440, which have been frequently called the "electron affinity" bands. An attempt has also been made to explain the continuous background.

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University Chemical Laboratories,
University of the Punjab,
Lahore, India.

CXXVII. *The Measurement of Sound-absorption in a Room* *. *By* Vern O. Knudsen, *Ph.D., Assoc. Prof. of Physics, University of California at Los Angeles* †.

I. *Introduction.*

THE fundamental differential equation for the distribution of sound in a room is ‡

$$V\frac{\partial I}{\partial t}+\tfrac{1}{4}vaI=E, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V is the volume of the room, I the average density of sound energy in the room, v the velocity of sound, a the total absorption of the room and its contents, and E the uniform rate of emission of sound energy from the sound source. The solution of (1) yields two equations which suggest practical methods for the determination of a. The first and simpler of these equations, which applies to the steady state when the rates of emission and absorption are equal, is

$$a=\frac{4E}{vI_0}t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* A part of this investigation was presented to the American Physical Society, March 5, 1927. (See Abstract, Phys. Rev. xxix. p. 753 (May 1927).)

† Communicated by the Author.

‡ G. Jaeger, "Zur Theorie des Nachhalls," *Akad. Wiss. Wien, Sitzungsberichte*, May 1911, p. 120. (See also E. A. Eckhardt, "Acoustics of Rooms," 'Journal of the Franklin Institute,' June 1923, p. 799; and E. Buckingham, "Theory and Interpretation of Experiments in the Transmission of Sound through Partition Walls," Scientific Papers of the Bureau of Standards, No. 506, May 26, 1925.)

where I_0 is the average maximal steady state value of the density of sound energy in the room. The second of these equations, which applies to the decay of sound in a room after the source has been stopped, is

$$I = I_0 e^{-\frac{va}{4V}t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The somewhat similar equation for the growth of sound in a room is also serviceable but not so convenient as the one for the decay. Equation (3), which gives the rate of decay of sound in a room, suggests two methods for determining a: (1) measurement of oscillograms of the decadent sound, or (2) measurement of the time required for a sound to be reduced to a known fraction of its initial steady state value. This latter method is the one chosen and developed by W. C. Sabine, and it has been used almost exclusively by all subsequent investigators. It is customary to use the ear as the detector in these measurements. The observer stops a tone of predetermined intensity (usually about one million times the minimal audible intensity) and measures the duration of audibility.

II. *Advantages and Limitations of the Different Methods for Measuring* a.

The simplicity of equation (2) makes it appear as a direct and an attractive means for determining a. It is necessary to measure only E and I_0, and substitute their values in (2). This is similar to the determination of electrical resistance by the voltmeter-ammeter method—the rate of sound emission corresponds to the e.m.f., and the average intensity I_0 corresponds to the current.

It is easy to modify (2) into a more useful form for laboratory measurements. Thus, by making two sets of measurements in the room, one with the room as it is to be tested and another with a known amount of absorption added to the room, it becomes unnecessary to know the rate of emission of the source, provided it remain constant for the two sets of measurements. The equations for these measurements are obtained from (2). Suppose measurements of I_0 be made in the room as it is to be tested. Then

$$a = \frac{4E}{vI_0}.$$

Now suppose a known amount of absorption a' has been

added to the room, by opening windows or by other means. Then

$$a + a' = \frac{4E}{vI'_0},$$

where I_0' is the resulting steady state intensity of sound in the room. Whence,

$$a = \frac{a'}{I_0/I'_0 - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

with I_0 and a known, E can be determined from (2) and its value used in all subsequent measurements, either in the same room or in other rooms, provided, of course, that E remain constant.

This method of determining the absorption of a room has a number of obvious advantages:—

1. The measurements are all instrumental, and thus independent of the ear of an observer.
2. The error in determining the absorption of a room is the same as the error in measuring the average intensity of sound in the room, and with suitable apparatus it should be easy to reduce this error to one per cent. or less.
3. The disturbing effect of residual noise in a room can be made negligible. If the intensity of the test tone be one thousand times as great as the intensity of the residual noise in the room, the noise introduces an error of only one-tenth of one per cent. It is an easy matter to produce test tones of this required intensity in an average room. Elaborate sound insulation, or the making of the measurements during the quiet part of the night, is thus obviated.

The method of measurement appears simple and precise, and, indeed, would be, were it not for the difficulties encountered in determining the average value of I_0. These difficulties were set forth lucidly by W. C. Sabine in one of his early lectures given at the Sorbonne in the spring of 1917*. The difficulties are of two sorts: first, the reflexions from the walls produce an interference pattern in the room with pronounced maxima and minima; and second, the rate of emission of the sound source is influenced

* W. C. Sabine, 'Collected Papers,' pp. 277–279. This is a free translation from notes which he prepared for one of the lectures.

by the interference pattern. If the vibrating source is situated at a maximum, it will experience difficulty in imparting any additional motion to the surrounding air. Or, if the vibrating source be situated at a minimum, it will impart an excessive motion. Sabine cites an instance in which the introduction of a large amount of acoustic felt in a room actually increased the loudness of the test tone; whereas, according to expectations from equation (2), the intensity should have been reduced to one-third of its initial value. Other workers in the field of sound, including the writer, have experienced similar "anomalies" in sound-intensity measurements. It is necessary, therefore, to thoroughly "mix" the sound in a room if reliable measurements of average intensity are to be made. W. C. Sabine introduced a large rotating steel vane into the sound chamber, which continuously shifts the sound interference pattern. This suffices for reverberation measurements. Eckhardt and Chrisler,* at the Bureau of Standards Sound Laboratory, use a rotating variable-frequency source of sound. Such devices help greatly to provide a uniform distribution of sound in a room, but even under these conditions it is necessary to make many measurements in all parts of the room in order to determine the average intensity of sound. The difficulties in making these measurements have been realized by Sabine and his successors, and for that reason practically all measurements of the sound-absorption of a room have been made by the reverberation method. The difficulties, however, do not seem insurmountable, and the simplicity and directness of utilizing such intensity measurements for the determination of the sound-absorption of a room have always appealed to the writer. Just what success may be anticipated from the use of this method will be indicated by the experimental part of this paper.

Equation (3), which expresses the law of decay of sound in a room, indicates that the absorption of a room can be determined by measuring the rate of decay. Perhaps the most obvious method for determining the rate of decay is to obtain oscillograms of the decadent sound. Suppose the curve in fig. 1 be the envelope of a typical oscillogram. If the ordinates in fig. 1 be measured for successive intervals of time, t', the ratios of corresponding ordinates separated by the same time-intervals will be constant. Let I'_0/I' represent the constant ratio of any ordinate to a successive

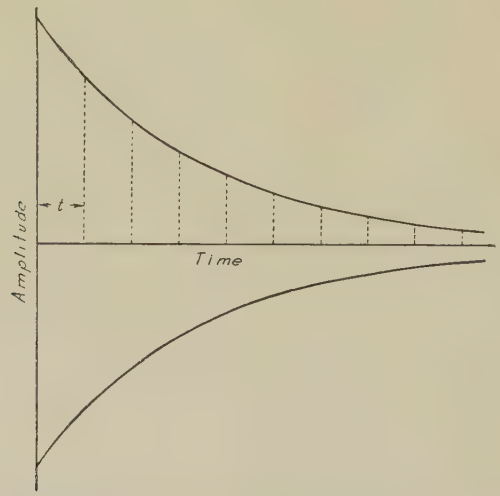
* 'Scientific Papers of the Bureau of Standards,' No. 526, April 28, 1926.

one t' seconds later; then the absorption of the room is given by

$$a = \frac{4V}{vt'} \log_e \frac{I'_0}{I'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the actual oscillograms the ordinates will represent the pressure-amplitude of the sound and not the intensity I, which is proportional to the square of the amplitude. I'_0/I' is therefore the square of the corresponding ordinates measured on the oscillogram.

Fig. 1.



Curve giving an ideal representation of how sound dies away in a room. The rate of decay furnishes a means of determining the total absorbing power of the room.

The advantages of this method of determining the absorption of a room are :—

1. The measurements are made from a photographic film, and can be made as slowly and accurately as desired. The oscillogram is thus a compact, permanent record, which can be filed for future reference.
2. The error in determining the absorption is proportional primarily to the logarithm of the intensity ratio I'_0/I' and therefore should be very small.
3. It is an absolute method, and no calibrating is required.

There are two limitations to this method for determining a. First, the decay is not uniform. The interference pattern in the room is pronounced and is in a state of rapid change ; successive maxima and minima are presented to the detector, and consequently the oscillogram is a complicated record of the decay of sound. After the source of sound has been stopped the residual sound becomes more and more uniform, but the successive maxima and minima are not completely eliminated.

The second limitation to this method comes from the interfering effect of any noise in the room. Since the residual decadent sound in the room becomes more and more uniform, the terminating portion of the oscillogram is best adapted for measurements. Hence any extraneous noise in the room would be superposed upon the decadent sound. This requires a relatively quiet room.

The two methods for determining a which have just been outlined have probably been considered by W. C. Sabine and subsequent workers, but have been abandoned because of the inherent difficulties arising from the sound-interference pattern in a room. These difficulties have been discussed, and, as will be shown later, special devices must be used to overcome them.

Sabine's investigations led him to adopt a third method for determining a. This is known as the reverberation method. It is necessary to have a source of sound, the rate of emission of which, E, can be varied by a known ratio. Then, if the duration of audibility of the residual sound for two values of E be determined, a can be calculated. Thus, let E_1 and E_2 be the rates of emission of the source, the ratio E_2/E_1 being known. (Sabine used one and four identical organ-pipes, separated from each other sufficiently to neglect mutual coupling, so that the four pipes emitted four times as much energy as one pipe. A suitable loud-speaker, actuated by a filtered oscillator current, can be used to advantage.) Let t_1 and t_2 be the durations of audibility of the two sources having rates of emission of E_1 and E_2 respectively ; and let I_m be the minimal audible intensity for an observer in the room. Then, since the intensity ratio, I_2/I_1, for the steady state, is equal to the ratio of the rates of emission of the source, E_2/E_1, it follows from (3) that

$$I_m/I_1 = e^{-va/4V\,t_1} \quad \text{and} \quad I_m/I_2 = e^{-va/4V\,t_2}.$$

Whence, by division and solving for a,

$$a = \log_e E_2/E_1 \; 4V/v(t_2-t_1). \quad . \quad . \quad . \quad . \quad (6)$$

In the organ-pipe experiments of Sabine, E_2/E_1 is usually four, the number of pipes used. In experiments using a loud-speaker as the source, E_2/E_1 can and should be at least one hundred. The only measurements necessary, besides V, the volume of the room, and v, the velocity of sound, are t_1 and t_2, which can be determined by the ear and a suitable chronograph. It is an advantage to have E_1 and E_2 as large as possible, as this increases the accuracy in measuring t_1 and t_2. It is an even greater advantage to have the ratio E_2/E_1 large, since this will reduce the error in the difference t_2-t_1. This method for determining a will yield fairly accurate results, provided a large number (at least fifty) of measurements of t_1 and t_2 are taken, and provided further that the test-room be completely free from noise.

The reverberation method has the following advantages :—

1. The decadent sound in the room, after the source has been stopped, becomes more and more mixed up as time goes on, so that near minimal audibility the intensity is nearly uniform in all parts of the room.
2. The pertinent measurements consist simply of time-measurements, usually of two or more seconds duration.
3. The apparatus requirements are simple—a standard source of tone, with means for adjusting the intensity, and a suitable chronograph comprise the necessary apparatus.

There are, however, a number of limitations to the reverberation method, and some of them are objectionable or difficult to control. There is an inherent error in judging just when the sound has reached minimal audibility. Two elements contribute to this error: first, the poor sensibility of the ear to small changes of intensity near the threshold of audibility; and second, the actual fluctuation of intensity resulting from the interference pattern in the room. Under ideal conditions, the smallest discernible change of intensity near minimal audibility is approximately 30 per cent *. Under actual working conditions, a change of about 50 per cent. would be nearer the practical limit. This would appear, on first thought, to be a serious source of error; but for a tone of usual intensity, that is one having an intensity of one million times the minimal audible intensity, the error in the measurement of t would be approximately 5 per cent.

* V. O. Knudsen, "Sensibility of the Ear to Small Differences of Intensity and Frequency," Phys. Rev. (ser. ii.) xxi. p. 84 (1923).

The actual fluctuation of intensity resulting from the ever-changing interference pattern also introduces an error in the observer's judgment of minimal audibility, the magnitude of which depends upon the nature of the room and the experimental equipment. The rotation of a large reflecting surface in the room, as is used by Paul E. Sabine in the Riverbank Laboratories, minimizes this error. However, measurements of t in an ordinary room, without a rotating reflector or other means for "mixing" the decadent sound, would be subject to an error of 5 per cent. or more. The errors arising from the poor sensibility of the ear and the interference pattern will be regularly distributed, and therefore, by taking an appropriate average of a large number of separate measurements (as many as fifty are usually made), satisfactory results can be obtained.

A more serious limitation to the reverberation method for measuring a is the necessity for absolute quiet in the test-room. The masking effect of any slight residual noise upon a feeble tone approaching minimal audibility is sufficient to introduce objectional errors in the measurement of t*. Since a noise comprises almost a continuous spectrum of all audible frequencies, it is capable of producing a masking effect upon a tone of any pitch. Even a very feeble noise of only 5 to 10 S.U.† would be sufficient to introduce an error of nearly 10 per cent. in the measurement of t. Noises of this loudness are prevalent in many rooms which are regarded as practically quiet. The limitations resulting from noise can be removed by providing a sound-proof test-room, or by choosing the quiet hours of the night, if there be any, as was done by W. C. Sabine. But the rooms in which absorption measurements are to be made are not always sound-proofed, and the task of making routine measurements between midnight and 4 A.M. is not attractive.

Another objection to the reverberation method is the use of the observer's ears as a most important part of the apparatus. Although a trained observer becomes adept at judging

* See article on "Auditory Masking of One Pure Tone by Another and its Probable Relation to the Dynamics of the Inner Ear," by R. L. Wegel and C. E. Lane, Phys. Rev. xxiii. p. 266 (Feb. 1924).

† This unit of loudness, proposed by telephone engineers, is gaining prestige among acoustic investigators. The loudness of a sound is expressed in S.U. by the formula:

$$\text{S.U.} = 10 \log_{10} \frac{I}{I_m}.$$

I is the intensity of the sound and I_m is the intensity at the threshold of minimal audibility.

just when the decadent sound has reached his minimal threshold of audibility, he is not infallible. There are a number of factors, such as judgment, attention, fatigue, reaction time in closing or opening the key associated with the chronograph, and actual change of hearing-sensitivity, all of which introduce errors in the measurement of t. The human element in the reverberation method for measuring the absorption of a room is probably its greatest weakness. Confidence in the accuracy of any measurements is increased if they can be made independently of fallible judgments of the sense organs. Anyone who has made reverberation measurements is certain to realize the limitations imposed by the use of his ear in judging just when a sound has reached minimal audibility, especially if there be any disturbing noise in the room.

The reverberation method, besides having the limitations mentioned, is laborious and slow, and requires the utmost care and patience on the part of the observer.

Finally, the method becomes very inaccurate in rooms having a short time of reverberation. For example, attempts to measure t in a theatre with carpeted floors and upholstered seats, in which t may be less than 1·5 sec., are most unsatisfactory.

But in spite of these limitations, the reverberation method is capable of yielding very useful results, accurate to about 1 per cent. under the most favourable conditions, and about 5 per cent. under conditions more commonly met with in the average room. The most fundamental data and principles in the field of architectural acoustics have been obtained by this method, and in the past it has afforded the only means for investigating the important problem of reverberation in auditoriums.

III. *Experimental Methods and Results.*

The object of the experimental part of the present investigation is to develop a simple and accurate method for determining the absorption of a room ; a method which will be free from the objectionable limitations of the reverberation method. Specifically, this investigation aims to determine whether the first two methods for determining a, discussed in the previous section, can be developed into practical laboratory methods. The main effort has been directed toward the development of the first method, that is, the determination of a by intensity measurements. For brevity, this method will be called the intensity method.

The method depending on measurements of oscillograms of the decay of sound in a room will be called the oscillograph method. The method depending upon measurements of duration of audibility will be called the reverberation method.

The experimental results presented in this paper are only of a preliminary nature, but they seem to indicate conclusively that there is at least one method of measuring a which can be freed from the limitations of the reverberation method, and which also can be made simple and accurate.

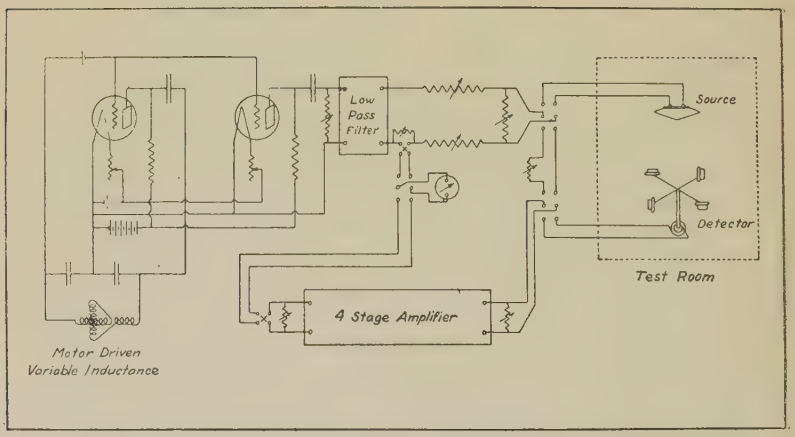
The first experiments on the intensity measurements, which were begun more than three years ago, indicated the nature of the difficulties described by W. C. Sabine in his 1917 Sorbonne lectures. Measurements were attempted using a loud speaker as a source of sound, and an electromagnetic telephone receiver and an amplifier as a detector. A single frequency of 512 d.v. was used. It was anticipated that an average value of the intensity would be obtained by taking a sufficiently large number of measurements, provided both the source and the detector were successively moved to representative parts of the room. For every position of the source a series of intensity measurements was obtained. The method indicated some promise of accuracy, but was abandoned because it was so laborious.

These initial experiments suggested the desirability of "mixing" or "stirring up" the sound in the room so that the interference pattern at any point in the room would shift between extreme limits of maxima and minima, and shift rapidly and continuously. All such devices as a rotating source, a rotating or oscillating detector, the use of as many as fifty detectors, distributed throughout the room, and a continuous change of frequency between two frequency limits, were employed in various combinations. The arrangement which worked most satisfactorily can be described by referring to fig. 2, which is a schematic diagram of the apparatus and electrical connexions. The oscillator is a Colpitts' circuit with a variable rotating inductance in the tuned circuit. With properly chosen values of inductance and capacitance in the tuned circuit, the oscillator generates an alternating current the frequency of which varies continuously with the rotation of the inductance, between 408 and 629 d.v. per second. The movable coil of the inductometer rotates at a constant speed of about two revolutions per second, so that the frequency periodically varies from 408 to 629 d.v. and back again to 408 d.v. A low-pass filter in the output of the oscillator is used to

eliminate the undesirable harmonics, and the current, thus purified, goes to a measuring circuit and thence either to the loud-speaker * in the test room, for producing the source of sound, or to the input of an amplifier, for calibrating the amplifier.

Two different types of detector were used. One, indicated in fig. 2, consisted of four electromagnetic telephone receivers, suitably mounted on a vertical shaft which was rotated by means of a phonograph motor. The receivers, mounted at different levels, thus are made to rotate in circles of about 4 feet diameter, with a speed of about 40 r.p.m. A second detector consisted of a single condenser trans-

Fig. 2.



Schematic diagram of the circuit and apparatus used for determining the average intensity of sound in a room.

mitter, rotated as a conical pendulum, with a swivel arrangement which eliminated all moving contacts.

The e.m.f. generated by either detector is amplified (four stages were used with the four receivers as detector, but

* Both the electromagnetic and the electrodynamic types of loud speaker have been used for the sound source. Davis & Fleming (Phil. Mag. ii. p. 51, July 1926) have shown that the electrodynamic type is the better suited for producing a constant source. This agrees with the findings of the writer. However, in most of the tests, a Western Electric electromagnetic cone type was used. This was used to avoid the resonant effects of horns associated with the available electrodynamic loud speakers. The constancy of the sound source with both types of loud speaker was maintained by frequent calibrations of the set-up under identical conditions.

three stages were sufficient with the condenser transmitter) and then measured with a thermo-couple and galvanometer. In order to eliminate errors arising from any possible changes of the amplification constant of the amplifier, the latter is calibrated for every measurement of the acoustically generated e.m.f.* The amplifier, the input leads, and the detector are shielded so as to prevent stray induction from reaching the amplifier.

The periodic variation of the frequency of the source and the rotation of the detector provide a satisfactory means of obtaining an average value of sound intensity at a certain locality in the room not too near the source. The variation of frequency serves the double purpose of "mixing" the sound pattern near the detector and also near the source. The latter is necessary to assure a constant rate of emission from the loud speaker. Since the frequency changes more than 50 per cent., the interference pattern at any point in the room will pass through all phases of intensity from local maxima to local minima.

The loud-speaker is located near the ceiling of the test room. A screen is placed between the source and the detector in order to shield the detector from the direct radiation from the source, In each series of measurements the detector is placed successively at eight different stations in the room. Four of these stations are about 4 feet above the level of the floor and near the four corners of the room. The other four stations are elevated about 7 feet above the floor. The separate measurements at the eight different stations, for a given condition of the room, do not differ among themselves by more than 10 per cent. The average of the eight measurements is taken to represent the average intensity of sound in the room. When the room is tested again with a different amount of absorption in it, the detector is placed in the same eight positions or stations.

The test room in which most of the measurements have been made is a reinforced concrete sound laboratory, 18 ft. × 18 ft. × 16 ft. high, furnished through the kindness of the Celacoustic Corporation of Los Angeles. The room has no windows and only one door. The loud-speaker and detector were the only equipment in the test room. The oscillator, the amplifier, and the measuring apparatus were in a separate room.

* The method of measurement is essentially the same as that used by the Bureau of Standards. See Bureau of Standards Scientific Paper No. 526, "Transmission of Sound of Some Building Materials," by E. A. Eckhardt and V. L. Chrisler.

Measurements by the Intensity Method using an Electromagnetic Cone Type Loud-Speaker as Source and Four Rotating Electromagnetic Receivers as Detector.—In these tests the absorption in the room was supplied by an acoustic plaster applied to the walls and ceiling. Tests were begun in the room with all four walls and the ceiling plastered. Then the acoustic plaster on two walls was stripped off and the room again tested. This was repeated with the acoustic plaster removed from all four walls. Finally, the room was tested with all of the acoustic plaster removed, that is, with walls, floor, and ceiling in concrete. The total absorption in the room, under each of the four different conditions, was determined both by the reverberation method * and by the intensity method. Many separate measurements of the absorption of the empty room, using the reverberation method with a tone of 512 d.v., had been made in previous work, and it was felt, therefore, that this absorption (25·0 units †) should be used as the most accurately known datum. All other calculations of a, by the intensity method, are based upon the assumed correctness of this datum. A summary of the results of the tests is given in Table I.

Table I.

Condition of Room.	a by Reverberation Method (512 d.v.).	Square of Input e.m.f. (in m.v.)[1].	a by Intensity Method (408–629 d.v.).	Percentage Difference.
Walls and ceiling concrete	25·0 units	·851	25·0	
Two walls plastered .	48·2 „	·458	46·4	3·8
Four walls plastered .	105·8	·205	103·8	1·9
Walls and ceiling plastered	152·0 „	·144	148·0	2·7

[1] The actual intensity in the room was approximately 10^7 times minimal audibility.

* V. O. Knudsen, "Measurement of Reverberation using the Thermionic Tube Oscillator as a Source," Jour. Op. Soc. & Rev. Sc. Inst. xiii. pp. 609–612 (1926).

† A unit is 1 square foot of perfectly absorbing surface, as an open window. All units in this paper are based on the British System because of the general use of these units in buildings among English-speaking people.

The agreement between corresponding values of a is very satisfactory, and is of the order of the probable experimental error.

Two other similar determinations of different amounts of absorption in a room, one in the same test room and another in a smaller test room at the University, both gave good agreement between the values of a obtained by the reverberation method and by the intensity method. In the first instance the percentage difference was 3·0 per cent., and in the second ·8 per cent.

Measurements by the Intensity Method using an Electrodynamic Loud-Speaker as Source and a Condenser Transmitter as Detector.—In these tests the absorption in the room was controlled by placing on the floor different amounts of patented acoustic tile. The total absorption of the empty room and its equipment, but with no absorbing material on the floor, was now 28·3 units, as determined by the reverberation method for a tone of 512 d.v. The increased absorption of the room (it was only 25·0 units in the former series of tests) is accounted for by the presence of additional equipment for supporting and rotating the condenser transmitter. The coefficient of absorption of the patented acoustic tile was determined both by the reverberation and the intensity methods. The coefficients obtained by the two methods differed by only 2·0 per cent., the average value being ·433. With the use of these two data, 28·3 units for the absorption of the empty room and ·433 for the coefficient of absorption, measurements were made to determine the relation between the average intensity of sound in the room and the total absorption in the room, the activity of the source remaining constant. Different amounts of absorbing material, from 4 sq. ft. to 127 sq. ft., were brought into the test chamber, and the average sound intensity determined for each condition of the room *. The results of the measurements are given in Table II. The first column in the table gives the amount of absorbing material in the room. The second column gives the total absorption of the room obtained by adding the amount contributed by the absorbing material (the area S of the acoustic tile multiplied by the difference between the coefficients of the acoustic tile and the concrete it covered) to the absorption of the empty room. The third column gives the deflexion of the galvanometer connected with the thermocouple in the output of the

* The apparatus was sufficiently delicate to detect readily the addition to the empty room of a single square foot of the absorbing material.

TABLE II.

Absorption Material in Room (S).	a calculated from $a=28\cdot3+S(\cdot433-\cdot014)$ (512 d.v.).	Average Galvanometer Deflexion on Output Thermocouple.	Average Sound Intensity in Room.	a by Intensity Method (408-629 d.v.).	Percentage Difference in values of a.
Room Empty	28·3 units	14·25	$5\cdot00\times10^{7}$	28·3 units	
4 sq. ft.	30·0 „	13·34	4·68 „	30·2 „	+ ·7
16 „ „	35·0 „	11·13	3·91 „	36·2 „	+3·4
36 „ „	43·3 „	9·25	3·25 „	43·6 „	+ ·7
49 „ „	48·8 „	8·19	2·88 „	49·2 „	+ ·8
64 „ „	55·1 „	6·99	2·46 „	57·5 „	+4·5
81 „ „	62·3 „	6·42	2·25 „	62·8 „	+ ·8
100 „ „	70·2 „	5·61	1·97 „	71·9 „	+2·4
127 „ „	82·1 „	5·05	1·77 „	79·8 „	−2·8

amplifier. The calibration curve of the amplifier showed that this deflexion was accurately proportional to the square of the a.c. voltage input of the amplifier. It follows that these deflexions are proportional to the energy density of the sound in the test chamber, provided the amplification factor of the amplifier remain constant. The amplification factor decreased about 2 per cent. during this series of measurements, but the change was a gradual one. The recorded deflexions in the third column have been corrected for this slight change, and hence these numbers give a relative measure of the sound intensity in the room. The fourth column gives the actual average intensity of sound in the room, expressed in terms of minimal audibility. The intensity was determined in the case of the empty room by reducing the current through the loud-speaker to the point of inaudibility. All other values of intensity were obtained by assuming the intensity proportional to the deflexions given in the third column. The total absorption of the room, as recorded in the fifth column, is calculated from equation (2). The last column gives the percentage difference between the corresponding values of a in the second and fifth columns.

The results recorded in Table II. are shown graphically in fig. 3. The first point on the curve was obtained by plotting the sound intensity in the empty room, measured by the galvanometer deflexion, against the absorption of the empty room. Thus, from Table II., it can be seen that the ordinate of this point is 14·25 and the abscissa is 28·3. The other points on the curve were determined by assuming that the sound intensity in the room was proportional inversely to the total absorption of the room for a tone of 512 d.v. The curve, therefore, is a rectangular hyperbola. The actual observed intensities for different amounts of absorption in the room are indicated by the small circles.

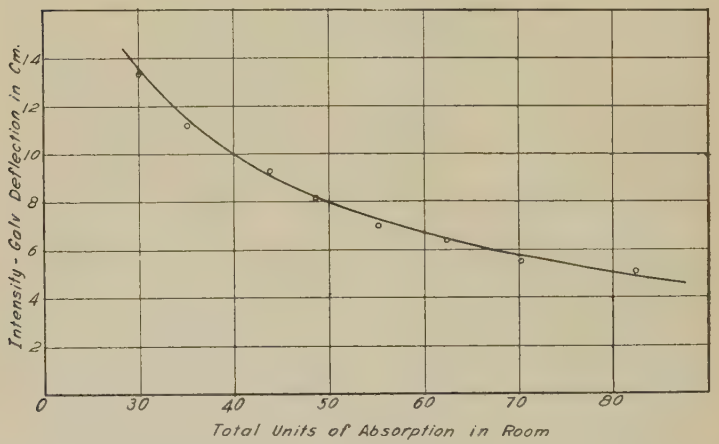
The close agreement between the observed intensities and the hyperbolic curve seems to support the general validity of the equation for the steady state of sound in a room, namely, that the average density of sound energy in a room is inversely proportional to the total absorption of the room.

In general, the measurements obtained with the electrodynamic loud-speaker as source and the condenser transmitter as detector were subject to smaller variations, and were altogether more satisfactory than those obtained with the electromagnetic loud-speaker as source and the four electro-

magnetic receivers as detector. The electrodynamic loud-speaker supplied a more nearly constant source of sound than the electromagnetic loud-speaker, and the condenser transmitter as a detector was both more sensitive and more nearly uniform in its sensitivity characteristic than the electromagnetic receivers.

The results obtained to date indicate that the intensity method can be utilized for accurate work in the determination of the absorption of a room or the coefficient of absorption of acoustic materials. The writer is at present designing a laboratory for testing purposes which will utilize this method. By reducing the size of the test

Fig. 3.



Curve showing how the average intensity of sound in a room depends upon the total absorbing power of the room. The curve gives the theoretical values of intensity, based upon the intensity being inversely proportional to the absorption of the room. The small circles indicate the measured values of intensity.

chamber and increasing the number of microphone units in the detector, it is believed that the absorption of the test chamber can be determined from a single reading of the galvanometer deflexion in the output of the amplifier. In future work it is also planned to design the oscillator so as to give a wide band of frequencies near 128 d.v. and another near 2048 d.v. Thus it will be possible to determine, both accurately and expeditiously, coefficients of absorption of acoustic materials for low, medium, and high frequencies. This is all that is necessary for most practical purposes.

Measurements by the Oscillograph Method.—Considerable work has been done in an effort to develop the oscillograph method for measuring a. The initial work began with a single frequency of 512 d.v. The oscillograms obtained indicate that the decay is very irregular, owing to the shifting interference pattern surrounding the detector. Measurements of the rate of decay on such oscillograms led to inaccurate results. They indicated only the order of magnitude of the absorption in the room, giving errors as great as 50 to 100 per cent. The best decay curves were obtained with the variable frequency source, 408 to 629 d.v., and the detector at rest. Oscillograms obtained in this manner gave values of a which differed approximately 10 per cent. from corresponding values obtained by the reverberation method. The results of two sets of measurements are given in the following table :—

TABLE III.

Condition of Test Room.	a by Reverberation Method.	a by Oscillograph Method.	Percentage Difference.
Empty.....	25·0 units	22·0 units	12·8 %
Floor covered with hairfelt, celotex, etc.	102·0 units	111·0 units	8·5 %

These preliminary results indicate that the oscillograph method probably could be developed into a precise and convenient method for measuring the absorption of a room. It appears necessary only to improve the technique of "mixing" the sound in the room so that the detector at every instant of the decay will respond to the average intensity of sound in the room. A more rapid fluctuation of the frequency of the source and a larger number of units in the detector should give more satisfactory oscillograms. This and other possible improvements will constitute a part of future work.

In conclusion, the writer gratefully acknowledges the co-operation of W. A. Munson and Lewis Delsasso in the experimental part of this work. He also wishes to record his thanks to the Calacoustic Corporation of Los Angeles for the use of the test chamber and for the labour of preparing the room for some of the measurements.

CXXVIII. *Cavitation in Screw Propellers.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the paper by Mr. J. Tutin, published in your July 1927 issue, there appears to be an error in equations (6) and (7) on page 21.

Taking equation (6), there are two ways of obtaining a momentum equation. First, we may consider the whole volume bounded by the curved lines in fig. 1. The inflow area is greater than A, say A′, so that the left-hand side of (6) should be $p_0A' - pA$. Further, the pressures on the curved sides should be included.

Alternatively, we may consider a cylinder whose section is that of the disk and with generators parallel to the central line of flow. In the momentum equation the left-hand side of (6) is now correct; but on the right a term should be added expressing the momentum of the fluid entering the cylinder through its sides due to the obliquity of the flow.

In either case, equation (6) is clearly incorrect, and by similar methods equation (7) can also be shown to be defective. The remainder of the paper is founded on these two equations, and, in my opinion, the author's conclusions are therefore erroneous.

Yours faithfully,

Naval Construction Dept.,
Admiralty, London, S.W.1.

L. WOOLLARD.

CXXIX. *Notices respecting New Books.*

The Problem of Physico-Chemical Periodicity. By E. S. HEDGES and J. E. MYERS, with a foreword by Prof. F. G. DONNAN. (Edward Arnold: London. Price 7*s.* 6*d.*)

IN this work, the authors give an extensive and connected account of periodic phenomena in chemistry and physics. They have collected a considerable amount of information bearing on this important and interesting subject, and from an examination of the data and from their own researches, put forward the suggestion that periodicity in chemical reactions is associated with surfaces in a metastable state.

Many examples of these periodic phenomena are cited in the text, *e. g.*, Dr. Holker's beautiful experiment on the periodic opacity of Wassermann "antigen" with sodium chloride as the electrolyte, the periodic decomposition of hydrogen peroxide, and the parallel periodicity of electropotential and the evolution of hydrogen by the dissolution of metals.

The bibliography and author index include nearly three hundred references to researches, from those of Fechner, Joule, and Quincke to the most recent contributions in the *Kolloid Zeitung* and other magazines, and the authors' papers in the 'Journal of the Chemical Society.'

Recent Advances in Organic Chemistry. By Alfred W. Stewart, D.Sc. Fifth Edition. Vol. i. pp. xiv + 387; vol. ii. pp. xiv + 382. (London: Longmans, Green & Co. 1927. Price 21*s.* net each.)

The fifth edition of Prof. Stewart's well-known account of recent advances in organic chemistry has been expanded into two volumes, an indication of the enormous amount of research which is in progress in this subject. In previous editions, a balance has been maintained between those portions of the subject on which general agreement has been reached and the newer lines of research. With the rapid development of the subject, some of the older material has had to be discarded in the preparation of new editions. The expansion into two volumes now allows some of this material—such as the chapters on addition reactions and unsaturation—to be included again.

The balance between the older and newer fields of organic chemistry is maintained by devoting one volume to each. The first volume, which is complete in itself, contains a survey of numerous fundamental problems of organic chemistry and is intended to cover the requirements of third-year students. It forms an introduction to the second volume, which contains an account of the most recent work in several well-selected fields which are of general interest. This volume is intended for Honours students and post-graduate workers. The subjects discussed include carbohydrate constitutions, the sesquiterpenes, rubber, the alkaloids, the anthocyanines, the chlorophyll problem, the depsides, abnormal valency, and applications of electronics. Several of the chapters are entirely new; the remainder have been revised or rewritten.

The first volume is prefaced by a historical chapter summarising the development of the subject up to the end of the nineteenth century. The second volume is prefaced by a similar chapter continuing the account up to the present time.

The output of original research in organic chemistry is so extensive that workers in and students of the subject will find Prof. Stewart's summaries of some of the more important problems invaluable both for study and for reference.

Spherical Harmonics. An Elementary Treatise on Harmonic Functions with Applications. By T. M. MacRobert, M.A., D.Sc. Pp. xii + 302 with 20 diagrams. (London: Methuen & Co. 1927. Price 15*s.* net.)

An account of the elements of the theory of spherical harmonics, in so far as it is required for applications to mathematical physics, is given in this volume. The treatment is sufficiently elementary for students with a good working knowledge of the calculus, but without knowledge of the theory of functions. The conditions for convergence of infinite series and for change in the order of terms are stated, but proofs of these conditions are not given. The use of spherical harmonics, Legendre functions, and associated Legendre functions, are illustrated by numerous applications to potential theory and to electrostatic problems. One chapter is devoted to Clerk Maxwell's theory of spherical harmonics.

Additional chapters are devoted to Fourier series, with illustrative applications to problems connected with the conduction of heat, and the vibrations of strings and membranes; and to Bessel functions with application to cylinder problems.

The volume contains all that will normally be required by the physical investigator, and the treatment is straightforward and elementary. It can be recommended to the student both for study and for reference.

The Measurement of Air Flow. By E. Ower, B.Sc., Hons. I., A.C.G.I. Pp. vii + 199 with 73 figures. (London: Chapman & Hall. 1927. Price 15*s.* net.)

The author in the course of his work at the National Physical Laboratory has experienced the need for a text-book on the subject of air-flow measurements, which frequently present serious practical difficulties to engineers. The volume under review has been written as a first step in the direction of meeting this need, and is intended to serve both as a text-book for students and as a work of reference for engineers engaged on matters such as fan engineering and the ventilation of mines and buildings.

With the practical needs in mind, the treatment is primarily of a practical nature. Mathematical discussions, where necessary, are of a sufficiently elementary nature to be followed without difficulty by those with a slight knowledge of the calculus. The design of Pitot and static tubes is discussed in detail, and the detailed dimensions of tubes which will record correct velocities without calibration are given. The use of Pitot-static tubes, as well as the plate orifice, Venturi tube and shaped nozzle for the measurement of the flow of air in pipes are described. Other methods of measuring air flow, by means of the vane anemometer (the theory of which is discussed in a very complete manner), the rate of cooling of heated wires, etc., are explained, and a chapter is devoted to a description of various types of manometer for the accurate measurement of small pressure-differences.

History of Science Teaching in England. By D. M. Turner, M.A. B.Sc. Pp.x+208. (London: Chapman & Hall. 1927. Price 7*s.* 6*d.* net.)

The introduction of science teaching into the Universities and into the schools, both secondary and primary, in England is of comparatively recent date, and was not achieved without considerable opposition from those who regarded science as a purely utilitarian subject without cultural value. The volume under review gives an interesting account of the gradual growth of the scientific spirit in England and of its reaction on the system of education, leading by slow stages to the present system in which the teaching of science is definitely incorporated, together with practical instruction.

It is of interest to note that the demand for science teaching resulted, in the first half of the nineteenth century, in the establishment of the Mechanics Institutes and night schools in which science teaching of a kind was given long before it was adopted as a general subject in the school or University Curriculum and before any discussion had been given to the question why science should be taught. The author discusses in an interesting manner different views which have been held as to the reasons for teaching science.

All students of pedagogy or of the history of science will find much to interest them in this volume.

CXXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 1016.]

March 7th, 1928.—Prof. J. W. Gregory, D.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'The Major Intrusions of South-Eastern Iceland.' By Hilda Kathleen Cargill, M.Sc., F.G.S., Leonard Hawkes, D.Sc., F.G.S., and Julia Augusta Ledeboer, M.Sc., F.G.S.

The main plutonic intrusions into the Tertiary plateau-basalts of Iceland were discovered some forty-five years ago in the south-east of the island, but little is known of their field-relations or petrology—and the present paper is a summary of the results obtained in the course of several summer visits to the more accessible localities.

The outcrops are scattered; the largest one (the Slaufrudal Stock) is elongate in plan, and its area covers $1\frac{1}{4} \times 4\frac{3}{4}$ miles. The relationship of intrusives to country-rocks (splendidly ex-

hibited in a series of cliff- and deep valley-sections) is a discordant one, the intrusions being stocks with steep-sided walls and domed roofs (not laccoliths as formerly suggested). The elongation of the stocks is parallel to the strike of the regional dykes, and intrusion clearly took place under, and was facilitated by, crustal tension. All intrusions are multiple: the common association is that of gabbro and granophyre. A horizontal layered structure of granite and granophyre is visible in the Slaufrudal stock, which seems to have grown by the injection of successive sills with intermittent subsidence of the replaced block.

The rocks belong to the calc-alkaline suite, and comprise in the order of differentiation gabbro-peridotite, gabbro, diorite, granodiorite, granophyre, granite, quartz-vein. This sequence may be correlated with the order of crystallization, which in the colourless minerals is:—plagioclase, potash felspar, potash felspar and quartz, quartz. No true orthoclase has been detected in the rocks—the 'potash felspars' are shown by analysis to contain about 40 per cent. of orthoclase. The plagioclase of the most basic rocks (gabbro-peridotites), which are poor in felspar, is more acid than that of the less basic and felspar-rich gabbros.

Eight new analyses are given. The suite, with the addition of granodiorite, is similar to that of the main plutonic intrusions of Tertiary age in Scotland. Comment is made on the absence of alkaline types in a region of 'Atlantic' tectonics.

The acid rocks exhibit two extreme textures—the graphic and the granitic, with intermediate varieties (semi-granophyres). The granophyres are richer in plagioclase and poorer in quartz than the granites which are quartz and potash-felspar rocks with 1 to 5 per cent. of hornblende. In the semi-granophyres the last residuum to crystallize shows granitic texture, and this is correlated with the fact that the granites are a later differentiate than the granophyres. The failure of the graphic intergrowth is ascribed to a diminished magmatic viscosity due to an increased content of volatile substances, with a consequent wider spacing of the centres of spontaneous crystallization, which inhibits the formation of the graphic fret.

The composition of the fret approximates to Vogt's 'granite eutectic', and the granophyres are considered to be eutectics, the excess of quartz in the granite residues being due to the presence of water.

In the whole Icelandic area intermediate rocks are relatively unimportant in bulk, the extrusives are dominantly basic, and the intrusives dominantly acid: this may be related to the superior mobility of the basic magma.

The absence of a sedimentary 'floor' in Iceland is noted, and in harmony with J. Barrell's hypothesis that the collapse of the North Atlantic basaltic plateau resulted from the intrusion of a basic magma, it is suggested that the preservation of the Iceland-Faeroes remnant is due to the intrusion beneath it of an acid magma.

March 21st, 1928.—Horace W. Monckton, Treas.L.S., Vice-President, in the Chair.

The following communication was read:—

'The Geological Structure of the Central Mendips.' By Francis Brian Awburn Welch, Ph.D., B.Sc., F.G.S.

The Central Mendips comprise a rectangular area roughly measuring 80 square miles, lying between the towns of Shepton Mallet and Cheddar on the east and west respectively. This area has been mapped on the 6-inch scale, applying the late Dr. A. Vaughan's zones for the purpose of investigating the structure.

As a whole, the Mendips consist of a west-north-westerly to east-south-easterly ridge, the structure being that of four periclines arranged en échelon. The cores of these periclines are of Old Red Sandstone age, with the Carboniferous Limestone Series succeeding.

The Central Mendips include the North Hill, the Pen Hill, and part of the Beacon Hill periclines. Of these, North Hill and Pen Hill are more or less anticlinal in structure; but the Pen Hill pericline has been much disturbed by extensive earth-movements. The pericline itself is overfolded, and its eastern portion is thrust northwards against the eastern end of the North Hill pericline, north-and-south faults bounding the thrust-block. Overfolding combined with thrusting appears to explain the non-appearance of *Cleistopora* Beds along the north side of the pericline.

A large syncline, which extends from Cheddar to Wells, has been thrust from the south against the southern limb of the North Hill pericline, while at one point a 'window' occurs in this syncline, revealing beds of the main hill-mass beneath the thrust. Parallel to this thrust, at Ebbor, a second great thrust is developed, isolated remnants of which are seen in the small hills north of Wells.

The inliers of Carboniferous Limestone age in the plain on the south point to considerable disturbance; but, owing to the covering of Triassic strata, relationship to the main hill-mass is not clear.

Earth-movements seem to have been directed mainly from the south, at first producing the ridge with periclines en échelon, and separated one from the other by normal synclines. Pressure continued, and appears to have been greatest in the Pen Hill region, where overfolding was developed. Finally overthrusting resulted, and large blocks of beds bounded by extensive north-and-south faults, formed at the time of the thrusting, were driven northwards.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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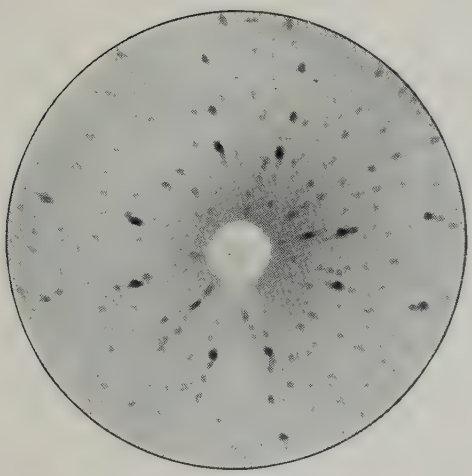
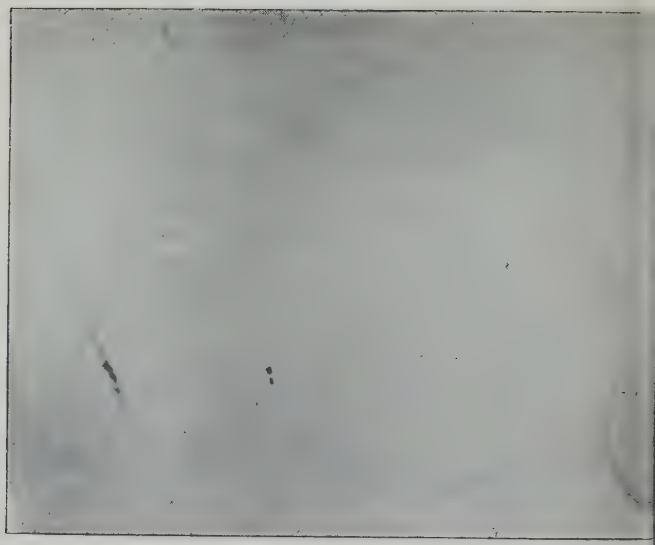


Laue Photograph of α-Manganese.

Mnl 4L



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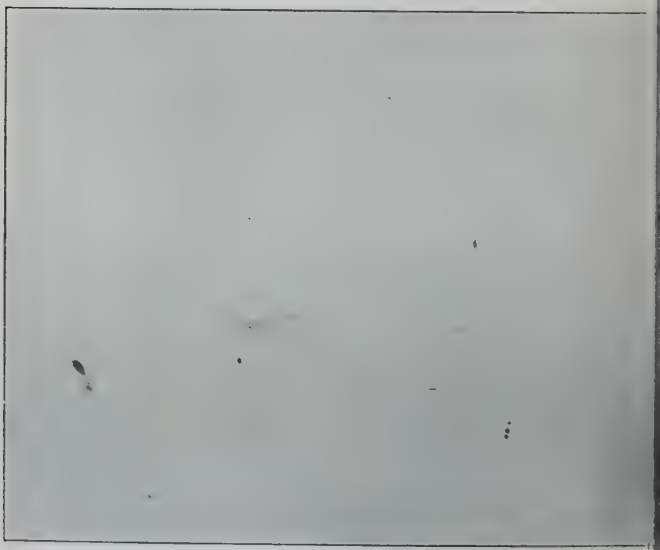
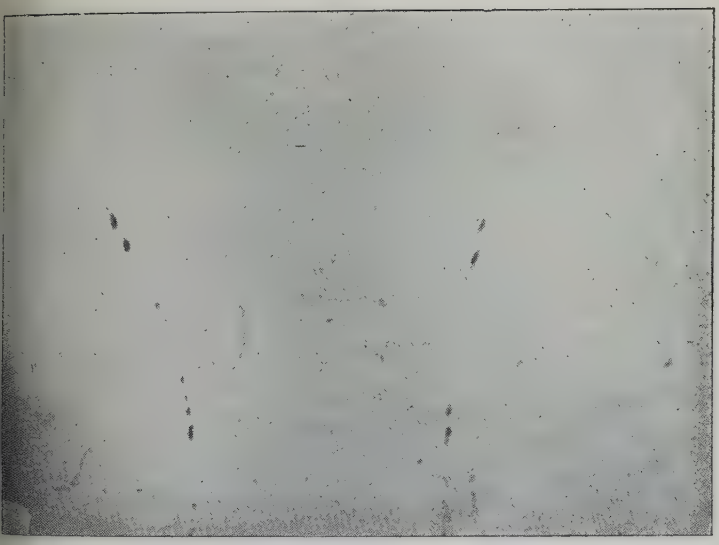


Mn1 4R



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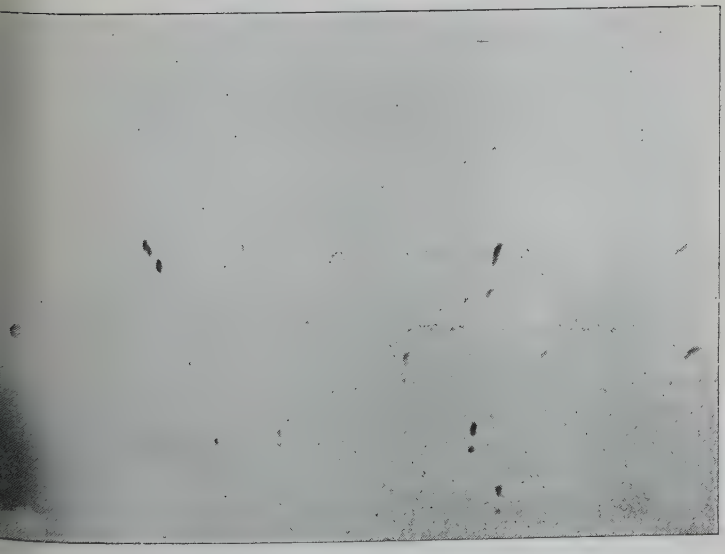
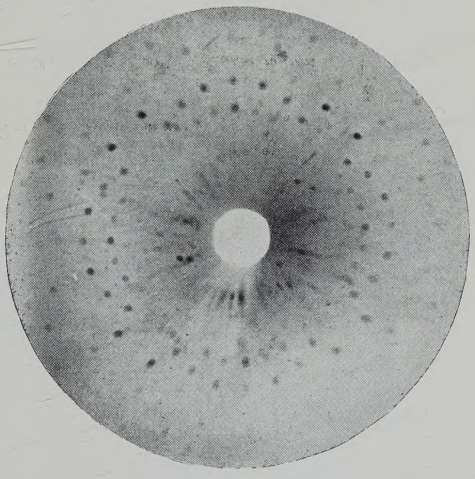


phs of α-Manganese.

FIG. 1.



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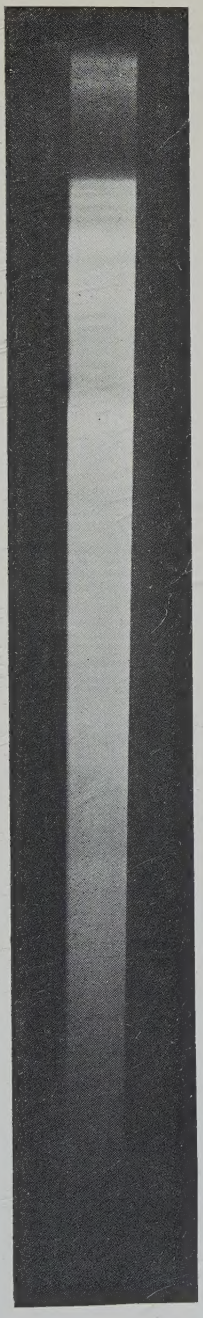

Tesla Luminescence Spectrum of Iodine.